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The Effect of Autoxidation on the Wettability of a Linoleic Acid Monolayer

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THE EFFECT OF AUTOXIDATION ON THE WETTABILITY OF A LINOLEIC ACID MONOLAYER

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ABSTRACT

Information about the structural characteristics of monolayers and how they are related to the resultant free surface energy is basic to an understanding of the mechanism involved in wetting. Although the wettability of saturated fatty acid monolayers has been studied extensively little work has been done on the wettability of unsaturated fatty acid monolayers. This study was undertaken in order to ascertain how autoxidation of a linoleic acid (cis, cis-9, 12-octadecadienoic acid) monolayer would affect the contact angle with water and methylene iodide. The objectives were to relate changes in the contact angle to the chemical changes taking place during autoxidation, and this in turn to the mobility of the oxidized molecules.

The effect of autoxidation on the contact angle with water depended upon the conditions of oxidation and the type of surface upon which the monolayer was formed. When autoxidation was carried out in dry air at room temperature, the products contained peroxide, hydroperoxide and possibly carbonyl functional groups. The U.V. spectra and reductive polarography indicated that the products were typical of solid-polymeric material produced during extensive autoxidation of bulk systems and the mobility of the molecules was thus decreased. On a glass surface with which the carboxyl group cannot react, this decrease in molecular mobility resulted in an increase in the contact angle. However, the increase was only from zero to a maximum of 56° because of incomplete oxidation and because the oxygen-containing functional groups were apparently accessible to the water. On the other hand, autoxidation in the presence of moisture produced material which was typical of the initial, monomeric products produced in bulk systems. Evidence was obtained for the 9 or 13-hydroperoxide of linoleic acid and also the equivalent keto-acid produced by dehydration of the hydroperoxide which are characteristic of the initial oxidation products. Thus, the mobility of the linoleic acid was evidently not greatly reduced under these conditions, and as a result the contact angle did not increase.

When the monolayer was formed upon a copper surface, the unoxidized molecules became quite immobile through reaction of the carboxyl group and the copper. As a result, the contact angle with water was about 92° after reaction between the carboxyl group and the copper was complete. Extensive autoxidation of the already immobilized molecules then decreased the contact angle evidently because of the introduction of oxygen-containing groups into the monolayer surface.

The contact angle between methylene iodide and the monolayer formed on a glass surface was not greatly affected by autoxidation. The angle was less susceptible to the motion of the unoxidized acid because of the size of the methylene iodide molecule and its low attraction for the glass. Thus, a decrease in the mobility of the acid molecules upon extensive autoxidation had less of an effect on the contact angle.

INTRODUCTION

The gradual loss of absorbency of paper products with time, self-sizing, is believed to be due to a deposition of polar-nonpolar molecules over the surface of the fibers (1). Such molecules, of which the fatty acids and their esters are representative, are thought to originate in the extractive portion of the wood that is still retained after pulping. When adsorbed they probably form a monolayer, the free surface energy of which is sufficiently low so as not to be wettable by water. Thus, knowledge about the structural characteristics of monolayers and how they are related to the resultant free surface energy is basic to an understanding of the mechanism of self-sizing.

The fat extractives of softwoods and hardwoods are composed of fatty acids, fatty acid glycerides, and resin acids (2). In many hardwood species, such as paper birch and trembling aspen, the unsaturated acids, particularly linoleic acid, make up a large fraction of the free fatty acid content. Although the wettability of saturated fatty acid monolayers has been studied extensively, almost no work has been done on the wettability of unsaturated fatty acid monolayers. Thus, a study was undertaken to investigate the wettability by water of linoleic acid monolayers, with special emphasis on the effect of autoxidation.

PRESENTATION OF THE PROBLEM

WETTING PHENOMENA

The wetting or nonwetting of a solid by a liquid is a function of the free surface energies of the solid and liquid. Adequate treatments of wetting phenomena are given in the texts by Adamson (3) and Davies and Rideal (4), and thus, only a summary will be presented here.

The excess energy of the surface of a solid or liquid arises from molecular fields of force which are not satisfied in all directions. For instance, in the interior of a solid or liquid an individual molecule is surrounded completely by other molecules, with the result that the molecular fields of force are satisfied in all directions. Upon bringing a molecule from the interior to the surface, the fields of force facing the vapor phase are not entirely satisfied due to the low concentration of the molecules in the vapor. Thus, energy must be supplied to bring the molecule to the surface. For example, if half the area surrounding a molecule in the surface is exposed to the vapor phase, the energy required would be approximately half the internal energy change upon evaporation. Surface energies are usually found to be less than this amount. Thus, for a single component system, the excess energy of a surface over that of the bulk phase arises from the gradient in density of the molecules at the boundary between the solid-gas, liquid-gas, or solid-liquid phases.

To rigorously calculate the excess surface energy using statistical thermodynamics requires detailed information regarding the potential and distribution functions of the molecules in both the bulk phases and the surface region. These functions can be estimated quite well for rare gas crystals where orientation effects are absent, and good agreement between the calculated and the measured

surface energy has been obtained for crystals of neon and krypton (5, 6). Similar treatments have been applied to liquids of symmetrical molecules with varying success (7-12). However, for most liquids the potential and distribution functions are neither known nor easily estimated, and so classical thermodynamics is employed to develop relationships between the properties of the bulk phase and the surface tension (13-15).

Gibbs (13) developed a relationship between the surface tension of a liquid, the pressures in the two phases and shape of the interface between them. The surface tension was defined in terms of the work required to create a unit area of interface between the liquid and vapor phases, keeping the temperature, volume, and concentration of the species constant during variation of the interface. This treatment leads to the following equation which is called the equation of capillarity

$$P_\alpha - P_\beta = \gamma(1/r_1 + 1/r_2) \qquad (1)$$

where

P_α, P_β = the pressures in the liquid and vapor phases, respectively;

r_1, r_2 = the principle radii of curvature of the interface;

γ = the surface tension of the interface.

By using Equation (1) it is possible to calculate the surface tensions of liquids without knowing the molecular configuration of the surface. However, the surface tension of a solid is not defined as readily since the forces involved are usually anisotropic, and, therefore, the surface tension could vary depending upon which direction the surface is extended. Also, the molecules may not be in an equilibrium position after extension. Thus, for solids, it has become the practice to define the surface tension as the partial derivative of the free energy of the

system with respect to the surface area at constant volume, temperature, and molecular species.

Solids and liquids can generally be classified as having either a high or low specific free surface energy. When the intermolecular forces arise from oriented dipole forces as well as dispersion forces, high energy surfaces are formed. However, when the molecular forces are primarily dispersion forces as in the case of hydrocarbon molecules, the surface is usually classed as a low energy surface. For example, the surface tension of water is 72.8 dynes per cm. at 20°C. whereas hexane is 18.4 dynes per cm. at 20°C. (16). The specific free surface energy of glass is estimated as being in the range of 135-170 dynes per cm. (17) as compared to paraffin which is estimated to be between 20-22 dynes per cm. (18). It is the relative magnitude of the specific free surface energies which determines whether or not a liquid will wet a solid surface.

In general, a liquid will wet a solid if the specific free energy of the liquid is less than that of the solid. When the specific free surface energy of the liquid is greater, it will form a finite contact angle with the solid, the magnitude of which depends upon the difference in the specific free surface energies. This generalization does not hold in all cases because of orientation effects at the interface and because adsorption of the liquid molecules may occur in such a manner that the high energy surface is transformed into a low energy surface (19). Because intermolecular forces extend over very small distances (e.g., the order of a few angstroms) only the few top layers of atoms determine the wetting properties of the surface (20). Thus, a high energy surface such as glass or cellulose can be changed into a low energy surface by adsorption of organic molecules such as stearic acid whose methyl group would be oriented away from the solid surface and toward the liquid.

The specific free surface energies of the solid-vapor, liquid-vapor and solid-liquor interfaces are related to the contact angle by the Young-Dupre Equation (21). Neglecting gravitational forces, the equation can be derived thermodynamically as shown in Fig. 1 (22). Referring to the following figure, for a finite variation of the system at constant volume, temperature and molar species, the derivation is as follows:

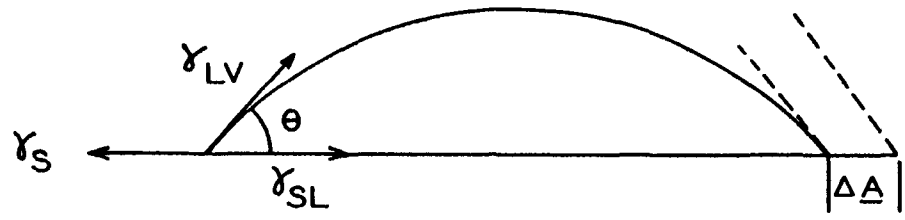


Figure 1. Liquid Drop Resting On A Solid Surface

$$\Delta F^S = \Delta A(\gamma_{SL}-\gamma_S) + \Delta A\,\text{cosine}(\theta-\Delta\theta)(\gamma_{LV}) \quad (2)$$

$$\Delta F^S/\Delta A = (\gamma_{SL}-\gamma_S) + \text{cosine}(\theta-\Delta\theta)(\gamma_{LV}) \quad (3)$$

In the limit as $\Delta A \rightarrow 0$, $\Delta F^S/\Delta A \rightarrow 0$ and Equation (3) becomes

$$\text{cosine}\ \theta = (\gamma_S-\gamma_{SL})/\gamma_{LV} \quad (4)$$

where

γ_S = specific free surface energy of the solid, in equilibrium with its vapor;

γ_{LV} = specific free energy of the liquid in equilibrium with its vapor;

γ_{SL} = the specific free energy of the interface.

Equation (4) can also be derived by taking into account all mechanical forces acting upon the system (e.g., gravity) (23). When this is done, an equation is obtained which contains a term for each mechanical force considered. By assuming the properties of the system to be continuous, the free energy change for a finite

variation of the system is zero. The term involving the surface tension forces leads to the Young-Dupre Equation. Other treatments also lead to the conclusion that Equation (4) is valid when considering all forces acting on the system (24, 25).

For ideal surfaces which are planar, homogeneous with respect to the atoms present in the surface and which are not altered by the wetting liquids, the contact angle is a convenient means of comparing the relative magnitude of the specific free energy of solid surfaces.

CONTACT ANGLES ON NONIDEAL SURFACES

In actual systems the criteria for an ideal surface are not always met, and the apparent contact angle may not be the true equilibrium contact angle. Because the contact angle is measured at some finite distance from the solid surface, the value obtained is affected by the topography of the surface. Also, specific interactions between the solid and liquid at the solid-liquid interface will decrease the interfacial free energy relative to that expected from the free energies of the liquid and solid. Finally, the solid surface may be altered by the liquid, or conversely, the liquid surface may be altered by the solid. The latter is frequently important in systems where contact angles are measured against monolayers of organic materials spread upon high energy surfaces. The effect of the topography of the surface and the effect of the changes in the solid and liquid free surface energies through contact of the two phases will be discussed in more detail.

NONPLANAR SURFACES

The importance of surface roughness and porosity on the contact angle has received considerable attention (26-29). The effect of surface roughness and porosity cannot be treated rigorously, but a quasi-thermodynamic treatment can

be developed (26). For a finite variation of the surfaces at constant temperature, volume, and mole species, the free energy has been described as follows:

$$\Delta F = (\partial F_{SL}/\partial a_{SL})\,(\partial a_{SL}/\partial A_{SL})\,\Delta A_{SL} + (\partial F_S/\partial a_s)\,(\partial a_s/\partial A_S)\,\Delta A_S + (\partial F_L/\partial a_L)\,(\partial a_L/\partial A_L)\,\Delta A_L \quad (5)$$

where

F_{SL} = free energy of the interface between the liquid and solid;

F_S = free energy of the solid-vapor interface;

F_{LV} = free energy of the liquid-vapor interface;

a_{SL} = actual area of solid-liquid interface;

a_S = actual area of the solid-vapor interface;

a_{LV} = actual area of the liquid-vapor interface;

A_{SL} = apparent area of solid-liquid interface;

A_S = apparent area of solid-vapor interface;

A_{LV} = apparent area of liquid-vapor interface.

Dividing through by ΔA_{SL} and since $(\partial a_{SL}/\partial A_{SL})$ equals $(\partial a_S/\partial A_S)$, in the limit as $\Delta A_{SL} \longrightarrow 0$ Equation (5) reduces to:

$$0 = (\partial a_{SL}/\partial A_{SL})\,(\gamma_{SL}-\gamma_S) + (\gamma_{LV})\text{cosine }\theta \quad (6)$$

where γ_{SL}, γ_S and γ_L are the specific free energies of the respective interfaces. Defining $(\partial a_{SL}/\partial A_{SL})$ as the roughness factor, r, cosine θ is described by the following equation:

$$\text{cosine }\theta = (r)\,(\gamma_S-\gamma_{SL})/\gamma_{LV} \quad (7)$$

On a rough surface the apparent contact angle presumably would be greater than the true angle when the latter is greater than 90°, and less when it is less than 90°.

However, this derivation is not rigorous because the Young-Dupre Equation was derived thermodynamically for infinitesimal variations. To be rigorous the contour of the liquid surface, as altered by the solid roughness, would have be taken into account.

Equation (7) can be generalized to yield an expression which includes the effect of porosity as well as surface roughness. The solid surface is considered to be heterogeneous consisting of homogeneous patches of two atomic groups having different specific free surface energies. Following the development of Equation (7), the relationship for the contact angle between a liquid and the heterogeneous surface can be written as shown below:

$$\gamma_{LV} \text{ cosine } \theta = (r_1)(\gamma_{S1}-\gamma_{SL1}) + (r_2)(\gamma_{S2}-\gamma_{SL2}) \tag{8}$$

where

$$r_1 = (\partial a_{SL1}/\partial A_{SL}) = -(\partial a_{S1}/\partial A_S);$$
$$r_2 = (\partial a_{SL2}/\partial A_S) = -(\partial a_{SL2}/\partial A_S)$$

If region two is the area of the solid surface which is porous, $(\gamma_{SL2}-\gamma_{S2})$ is equal to γ_{LV} and Equation (8) becomes

$$\text{cosine } \theta = (r_1)(\text{cosine } \theta_1) - r_2 \tag{9}$$

Thus, the porosity always increases the contact angle if a liquid-vapor interface is formed.

The geometry of the surface may also be altered by deformation of the solid by the surface tension forces of the liquid (30, 31). The component of the surface tension of the liquid defined by (γ_{LV}) sine θ must be compensated by an equal and opposite force directed into the solid phase. For such a force to exist, the solid

must be deformed around the periphery of the drop. However, for normal solids the modulus of elasticity is sufficiently great so that the deformation is negligible.

It is not easy to correct for errors arising from the roughness and porosity of the solid surface. However, their effect on the experimental results can be minimized by using reproducible surfaces which are as smooth as possible. The difference between the true angle and the measured angle can be kept to within 5 degrees by taking reasonable precautions (32).

SURFACES ALTERED BY WETTING LIQUIDS

The wetting liquids may alter the surface with which they come in contact in such a way that the specific free surface energy values in Equation (4) are not easily defined. Such a process involves transport of the liquid phase or solid phase or both simultaneously. Disruption and transport of the solid phase is frequently important in the case of monolayers of organic molecules spread upon high energy surfaces.

Low Free Surface Energy Solids

The specific free surface energy quantities in Equation (4) are written for the solid and liquid phases in equilibrium with their respective vapor phases. However, to be rigorous, the equation should be written in terms of the specific free energies in equilibrium with the vapor phase of the combined solid and liquid. The vapor of the solid probably would not alter γ_{LV}, but the liquid vapor could adsorb on the solid changing γ_S. Therefore, Equation (4) should be written as follows (33):

$$\text{cosine } \theta = (\gamma_{SV}-\gamma_{SL})/\gamma_{LV} \qquad (10)$$

where γ_{SV} is the specific free energy of the solid in equilibrium with the vapor of the liquid. Then if π equals $(\gamma_S - \gamma_{SV})$ Equation (10) becomes

$$\text{cosine } \theta = (\gamma_S - \gamma_{SL} - \pi)/\gamma_{LV} \qquad (11)$$

The magnitude of π is determined by the amount of the wetting liquid which is adsorbed on the solid surface. When the liquid makes a finite contact angle with the surface, the heat of adsorption, hence the amount adsorbed, is usually quite low. Thus, for low energy solid surfaces and high energy liquids, π is found experimentally to be negligible (34). At low contact angles where π is expected to be large, cos θ is a small function of θ, and π has to be very large in order to affect the measurement materially. Therefore, neglecting π would probably not introduce a large error.

Movement of the wetting liquid into the crevices of the solid surface can increase γ_S and thus lower the contact angle. Adam and Elliott (35) found that immersion of polythene in water for several hours lowered both the advancing and receding angles, the latter much more than the former. The authors believed that the water was entrapped in the polymer surface which increased γ_S and decreased γ_{SL}, resulting in an over-all decrease in the contact angle.

Monolayers of Organic Molecules On High Energy Surfaces

The penetration of the wetting liquid into monolayers spread upon high energy surfaces can influence the magnitude of the contact angle greatly (36, 37). Also, redistribution of the monolayer molecules may occur in such a manner that γ_{SL} and γ_{LV} will be decreased resulting in a decrease in the contact angle. γ_{SL} and γ_{LV} will decrease if the following occurs: (1) solution of the monolayer material in the liquid drop so that the surface of the high energy solid is exposed (38); (2) spreading of the monolayer molecules on the drop surface (39); (3) reorientation of the molecules in such a way that a high energy group is presented to

the wetting liquid (40). The latter is especially important with fatty acids because they contain both a hydrophilic group (i.e., the carboxyl group) and hydrophobic groups (i.e., the hydrocarbon chain). When in a monolayer, the acid molecules will normally orient with the carboxyl group toward, and the hydrocarbon chain away from the solid surface so that the free surface energy will be at a minimum. However, although the molecular forces extend only over distances of a few angstrom units, the mobility of the molecules (41, 42) necessitates a consideration of all the atomic groups when determining what intermolecular forces are influencing the contact angle.

Apparently, the extent the contact angle is affected by the above phenomena depends upon the concentration of the molecules on the surface, their solubility in the wetting liquid, the attraction between the carboxyl group and the high energy solid surface, and finally, upon whether the monolayer is in the liquid or solid state.

Bartell and Ruch (36, 37) investigated how the progressive depletion of monolayers of n-octadecyl and n-dodecyl amine adsorbed on platinum influenced the contact angle with a number of wetting liquids. If the specific free surface energies of the monolayer and the wetting liquid were similar, the manner in which the angle varied with the surface concentration of the amine depended greatly upon the shape of the liquid molecule. If the molecule was long and narrow as in the case of hexadecane, it diffused into the monolayer and became oriented with the methyl groups in the surface so as to fill in the gaps formed upon depletion. Thus, little change in the contact angle was noted until 50% of the monolayer was removed. At this point the hexadecane molecules were no longer oriented. This lack of orientation evidently lowered γ_{SL} and increased γ_S, and the contact angle decreased quickly to about zero. If the liquid molecule was spherical, orientation did not occur and the angle commenced to decrease when less of the monolayer was

removed. When the difference between the specific free surface energies of the liquid and the monolayer surface was large (e.g., with water), the effect of depleting the monolayer was not influenced as much by the size and shape of the molecule. Evidently, the large difference in the free energies prevented the water from diffusing into the monolayer and contacting the high energy solid surface.* As a result, the contact angle did not decrease until after 50% of the n-octadecylamine monolayer was removed. Furthermore, the angle decreased slowly upon further depletion, and complete wetting did not occur even after 90% of the monolayer was removed. Where the wetting liquid diffuses readily into the monolayer, the free surface energy of the monolayer may be increased by lateral movement of the liquid outside the periphery of the drop. Such a movement of the liquid would increase γ_S and therefore decrease the contact angle. In summary, the authors found that the extent to which the concentration of the molecules on the surface influences the contact angle depends upon the size and shape of the molecules of the wetting liquid, and the difference between the specific free surface energies of the monolayer and the wetting liquid. The attraction between the monolayer and the solid surface may also be important but this was not fully studied.

The solubility of the monolayer in the wetting liquid evidently can greatly influence the contact angle. Bigelow, et al., (38) studied how various pure organic liquids wet monolayers of n-octadecylamine, eicosyl alcohol, and batyl alcohol formed on a platinum surface. The higher the boiling point of the wetting liquid the less soluble was the monolayer in the drop. As the boiling point

*Unless the liquid diffuses to and wets the high energy solid, a liquid-vapor interface would be formed over the depleted areas. These areas would then tend to act as a pore and the contact angle would not be expected to decrease upon depletion [see Equation (9)].

decreased, the monolayer became more soluble and the contact angle was lowered greatly beyond that expected from the surface tension of the liquid. In some instances the depletion was so rapid and complete that an equilibrium contact angle could not be measured. Zisman, et al., (43) also found that n-alkanoic acids tended to dissolve monolayers of fluorinated acids. A large increase in the contact angle was noted when the n-alkanoic acids were saturated with the monolayer material. Evidently, the ability of the wetting liquid to solvate the hydrocarbon chain of the fatty acid determined the extent to which the contact angle was lower than expected.

Apparently, the magnitude of the attraction between the monolayer molecules and the solid surface is not very important in determining the contact angle with nonpolar organic liquids. For example, Shafrin and Zisman (44) found that hexadecane formed the same angle against an octadecylamine monolayer irrespective of whether it was on glass or platinum. However, if the wetting liquid is quite polar, the attraction between the monolayer molecules and the solid becomes very important. This is especially true of fatty acid monolayers. For example, Langmuir (40) found that the contact angle between water and a monolayer of oleic acid depended upon the solid surface on which the monolayer was formed. The angle was 18° on mica, 45° on glass, 65° on platinum, 70° on calcite, 82° on sphalerite, and 86° on galena. However, if care was taken to prevent the glass surface from being contaminated with heavy metal ions with which the carboxyl group could react, the contact angle was zero. In comparison, the contact angle was 55° when the monolayer was on a chromium surface.

Schacht, et al., (45) also found that the contact angle between water and a stearic acid monolayer was determined by the degree of attraction of the carboxyl group for the solid surface. After one minute of contact between the water and the stearic acid, the contact angle was 35° for the monolayer on mica, 47.5° on glass, and 104.5° on copper.

Shepard and Ryan (46, 47) found that contact angles between water and glycerol and a perfluorooctanoic acid monolayer were determined largely by the substrate as shown in Table I.

TABLE I

CONTACT ANGLES BETWEEN POLAR LIQUIDS AND PERFLUOROOCTANOIC ACID MONOLAYERS (44)

Solid Surface	Contact Angle, degrees Water	Glycerol
Glass	spread	spread
Platinum	46-85	46-81
Aluminum	61-77	58-90

Autoradiographs of radioactive perfluorooctanoic acid monolayers, after removing the liquid drops, showed that the monolayer was "desorbed" by the polar liquids, the greatest depletion being when the monolayers were on the glass.

Finally, Yiannos (48) determined the contact angle of water against mixed monolayers of stearyl alcohol and stearic acid spread on copper and silver surfaces. The stearic acid reacted with the copper surface while the stearyl alcohol did not. The equilibrium contact angle was a function of the percentage of stearyl alcohol in the monolayer being 71° at 100% stearyl alcohol and 104° at 100% stearic acid. When the mixed monolayers were deposited onto silver, (the carboxyl groups were found not to react with the silver over short periods of time) the contact angle was about 72° at all concentrations of the stearyl alcohol.

It is evident from the aforementioned data that the attraction of the carboxyl group for the solid substrate was very important in determining the magnitude of the contact angle with polar liquids and especially water. When the fatty acids were firmly attached to the solid surface so that $-CH_3$ groups formed a stable low free energy surface, the contact angle approached the value for water against

paraffin. When the carboxyl group could not react with the surface, a low energy surface apparently was not maintained and the contact angle decreased markedly. Langmuir (40) proposed that the molecules were reoriented so that the carboxyl groups were facing the water. The interfacial tension, γ_{SL}, would then be near zero and the contact angle would be lower than expected. Other authors have expressed similar views (46-48). Whether the overturning of the molecules is the only factor involved in the contact angle decrease has never been definitely proven. Seemingly, spreading of the fatty acid on the water surface or diffusion of the water into the monolayer could also be important contributing factors.

Apparently, the magnitude of the contact angle also depends upon whether the monolayer is in the liquid or solid state. The state of a monolayer is determined largely by the magnitude of the attractive forces between the hydrocarbon chain, assuming the carboxyl group cannot react with the surface, as shown by the work of Menter and Tabor (49). From electron reflection diffraction patterns, the authors determine at what temperature saturated fatty acid monolayers ceased to show an ordered structure. The temperature increased as the melting point of the acid increased. Thus, at room temperature very well-oriented monolayers with the hydrocarbon chains perpendicular to the surface were formed by acids whose chain length was greater than sixteen carbon atoms, e.g., palmitic acid. Below this chain length, the orientation became increasingly poor and was not observed at all for chains less than twelve carbon atoms long, e.g., lauric acid. Thus, the shorter chain acids exhibited a high degree of motion and the state of the monolayer can be compared to the liquid state in the bulk phase. The transition temperature for the change from the solid to liquid state of the monolayers was generally much lower than the bulk melting point of the acid* excepting when there was a chemical reaction between the carboxyl group and the solid surface. When there was a

*For example, lauric acid melts at 44°C., but the monolayer was disordered at room temperature.

chemical reaction, the transition temperature was equal to, or above the bulk melting point. Therefore, on a surface with which the carboxyl group cannot react, any fatty acid whose melting point approximates or is below room temperature will probably form a monolayer which is in the liquid state.*

Evidently, when the monolayer is in the liquid state, the contact angle is much lower than would be expected both for polar and nonpolar liquids. For example, Bigelow, et al., (38) found that as the melting point of the fatty acid decreased, the contact angle with hexadecane decreased. The hexadecane saturated with the monolayer material formed finite contact angles with stearic acid monolayers at room temperature, but did not form finite contact angles with oleic acid, elaidic acid, linoleic acid, or linolenic acid all of which were near or above their bulk melting points. The authors attributed the lack of oleophobic behavior of these latter monolayers to the presence of the double bond. They assumed that its presence decreased the van der Waals cohesive forces which prevented the molecules from adsorbing to form a monolayer with the $-CH_3$ groups outermost. If the attraction between the hydrocarbon chains of oleic or elaidic acids was increased by the introduction of a hydroxyl group to form ricinoleic or ricinelaidic acid, the monolayer then became oleophobic. Also, the contact angle with water is much lower than would be expected when the monolayer is above its melting point. Langmuir (40) found the contact angle with oleic acid and stearic acid monolayers on chromium to be 55 and 90°, respectively. When on a glass surface the angle is zero against the oleic acid and 105 to 70° on the stearic acid depending upon how long the drop is left on the surface before the angle is measured (48). Apparently, when the monolayer is on a nonreactive surface,

*The state of a monolayer spread upon an aqueous surface is also determined largely by the magnitude of the attraction between the hydrocarbon chains. As an example, lauric acid forms a liquid expanded film at room temperature while stearic acid forms a solid film.

diffusion of the water into the monolayer, redistribution of the monolayer molecules over the surface of the water, reorientation of the fatty acid, etc., become increasingly important as the liquid state is approached,* until finally the monolayer loses its ability to form a finite angle with the water. Evidently, the greater the attraction between the acid molecules the more stable will be the monolayer (48), the ultimate being when they are linked together through covalent bonds (51).

The foregoing discussion on wetting phenomena leads to deductions regarding the type of organic materials that would form hydrophobic monolayers and possibly contribute to the self sizing of paper. Thus, saturated fatty acids and glycerides of fatty acids which have high melting points, polar groups with a high affinity for the cellulose surface and finally hydrocarbon chains which can be so oriented that the $-CH_3$ groups form a low free energy surface, produce sizing when spread on cellulose surfaces (52). However, if the theory of Swanson and Cordingly (53) is correct, redistribution of the fatty material from the ray cells over the surface of the fibers will depend largely on the vapor pressure and/or spreading pressure of the fatty acid. Thus, the factors which are important in redistribution of the fatty acids will probably favor the formation of a monolayer of the unsaturated acids which are above or near their melting point at room temperature, such as linoleic acid.

A monolayer of linoleic acid would not be expected to be hydrophobic because the bulk melting point is below room temperature, and the attraction of the water for the cellulose surface would be about the same as that of the carboxyl group, unless esterification occurs. However, after being distributed over the cellulose

*As an example, the surface tension of water in equilibrium with a crystal of stearic acid resting on its surface decreases from about 73 dynes per cm. at 25°C. to 36 dynes per cm. at 71°C. (50).

surface, reactions occurring during autoxidation of the acid might increase the cohesive forces between the molecules through the introduction of oxygen groups into the hydrocarbon chain and also through the formation of covalent bonds. Such an increase in the cohesive forces might immobilize the linoleic acid molecules and produce a relatively stable low energy surface against which the water would form a fairly large contact angle. This possibility will be pursued further in the next section on the autoxidation of linoleic acid.

AUTOXIDATION OF LINOLEIC ACID

The oxidation of unsaturated fatty substances initially leads to oxygenated, monomeric derivatives which undergo addition, oxidation, or decomposition to form polymeric products. These secondary reactions are the basis for the setting of drying oils and result in the transformation of a liquid fatty acid or fatty acid ester film into a solid film which has the desirable protective qualities. The mechanisms of fat oxidation are essentially the same for all such systems, and thus, the reaction kinetics will be reviewed briefly.

KINETICS OF AUTOXIDATION

A complete review of the kinetics of autoxidation has recently been compiled by Lundberg (54), and only a brief summary will be presented here. The autoxidation of linoleic acid (cis, cis-9, 12-octadecadienoic acid) or some other unconjugated polyeonoic fat presumably proceeds through three stages although the only difference is in the relative rates at which a series of parallel reactions take place. The three stages are:

1. The induction period;
2. The primary oxidation period;
3. The secondary oxidation period.

The reaction proceeds through a free radical mechanism (55), and during the induction period little oxidation occurs because the free radicals are destroyed by impurities in the system. When a significant concentration of free radicals has been produced, oxidation of the unsaturated fatty acid begins. This primary oxidation marks the onset of hydroperoxide formation and conjugation of the double bond. The hydroperoxide is formed by oxidation of free radicals produced in the hydrocarbon chain, and conjugation of the double bonds accompanies this step. The third period, or secondary oxidation, is characterized by an accelerated breakdown of the hydroperoxides and the oxidation of the conjugated double bonds.

The kinetic theory which applies to the initial stages of the oxidation is very similar to the classical chain kinetics of vinyl polymerization (56-60). The reactions are divided into those occurring in the initiation, propagation, and termination of the free radicals.

Initiation* (production of free radicals):

$$\left.\begin{array}{l} \mathrm{ROOH} + h\nu \xrightarrow{k_1} \\ 2\mathrm{ROOH} \xrightarrow{k_2} \end{array}\right\} \mathrm{R}\cdot + \mathrm{RO_2}\cdot \qquad (12)$$

Propagation:

$$\mathrm{R}\cdot + \mathrm{O_2} \xrightarrow{k_2} \mathrm{RO_2}\cdot \qquad (13)$$

$$\mathrm{RO_2}\cdot + \mathrm{RH} \xrightarrow{k_3} \mathrm{ROOH} + \mathrm{R}\cdot \qquad (14)$$

Termination:

$$\left.\begin{array}{l} \mathrm{R}\cdot + \mathrm{R}\cdot \xrightarrow{k_4} \\ \mathrm{R}\cdot + \mathrm{RO_2}\cdot \xrightarrow{k_5} \\ \mathrm{RO_2}\cdot + \mathrm{RO_2}\cdot \xrightarrow{k_6} \end{array}\right\} \text{inactive products} \qquad \begin{array}{l} (15) \\ (16) \\ (17) \end{array}$$

*RH represents the linoleic acid and R· the acid free radical

Under mild conditions of oxidation,* the hydroperoxide (RO_2H) does not break down readily and most of the oxygen is present as the hydroperoxide. The chain length is then long and the reaction autocatalytic. Assuming a steady state concentration of free radicals, $\underline{k}_5^2$ equals $\underline{k}_4\underline{k}_6$, $(R\cdot)/(RO_2\cdot) = (\underline{k}_3)(RH)/(\underline{k}_2)(O_2)$ and the hydroperoxide is not decomposing, the rate of oxidation can be represented by the following rate equations:

$$-d(O_2)/dt = d(ROOH)/dt \tag{18}$$

$$-d(O_2)/dt = (k_3)(RO_2\cdot)(RH) \tag{18a}$$

$$-d(O_2)/dt = (r_i/k_6)^{1/2}(k_3)(RH)(k_2)(k_6)^{1/2}(O_2) \times 1/[(k_3)(k_4)^{1/2}(RH)+(k_2)(k_6)^{1/2}(O_2)] \tag{19}$$

Except where the reactivity of the fatty acid is large, the oxidation of the acid free radical is much faster than the hydroperoxide formation, and thus Equation (19) can be reduced to

$$-d(O_2)/dt = (r_i)^{1/2}(k_3/k_6^{1/2})(RH) \tag{20}$$

Under such conditions the rate of oxidation is independent of oxygen partial pressure. As an example, the oxidation of ethyl linoleate is independent of oxygen partial pressure above a partial pressure of 200 mm. of mercury at 45°C. For linoleic acid the partial pressure would be somewhat higher since it is about 1.35 times more reactive than the ethyl linoleate (61).

Under more severe conditions, such as high temperature and catalysis by metal ions and ultraviolet light, the decomposition of the hydroperoxide becomes important,

*Mild conditions of reaction would be room temperature, short times, and the absence of catalysts which break down the peroxides.

and Equation (18a) is no longer applicable (62). Assuming that RH remains constant, the rate of hydroperoxide formation and the rate of oxidation are as follows:

$$d(ROOH)/dt = (k_3)(k_1/k_6)^{1/2}(ROOH)(RH) - (k_1)(ROOH)^2 \quad (21)$$

and

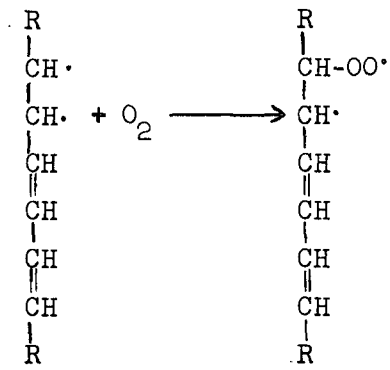
$$-d(O_2)/dt = (k_1/k_6)^{1/2}(k_3)(ROOH)(RH) \quad (22)$$

Equations (21) and (22) predict that a maximum concentration of hydroperoxide and a maximum rate of oxidation are obtained if the concentration of RH remains constant. If the decomposition of the hydroperoxide is unimolecular as when catalyzed by metal ions the same is true. The maximum concentration of the hydroperoxide is inversely proportional to the rate of decomposition of the hydroperoxide. However, the maximum rate of oxidation is independent of the breakdown of the hydroperoxides and depends only on the rate of formation of the hydroperoxide, the rate of termination of the peroxy radicals and the concentration of the fatty acid. Thus, metal ions, ultraviolet light and other activators do not change the mechanism of the reaction, but do decrease the time required to reach the maximum rate of oxidation.*

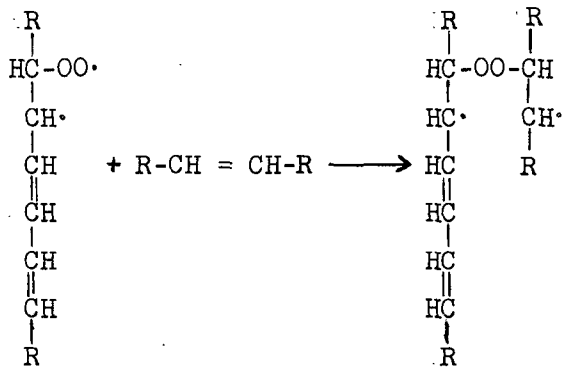
When the concentration of fatty acid is not in excess, the hydroperoxide concentration passes through a maximum (61, 62, 64, 65). The decrease in concentration is caused by an accelerated breakdown of the hydroperoxide by secondary oxidation products and by a loss of α-methylene hydrogen. The decrease in the peroxide concentration marks the onset of the secondary oxidation period. The

*Surfaces apparently activate the oxidation much in the same manner as do metal ions. George and Robertson (63) found that the rate of oxidation of tetralin was increased by introducing powdered materials into the reaction flask. A maximum in the effective surface area was reached over which an additional increase had no effect.

kinetics of the secondary oxidation period have not been developed due to the large number of possible reactions. However, in addition to more rapid decomposition of the hydroperoxides, oxygen can attack directly the conjugated double bonds produced during the formation of the hydroperoxides (61, 65). In the oxidation of eleostearate (61, 66) the amount of triene conjugation lost and the amount of diene conjugation formed were both proportional to the oxygen consumed. Thus, Allen and Kummerow (66) proposed that the oxygen added by a diradical mechanism which is as follows:



(23)

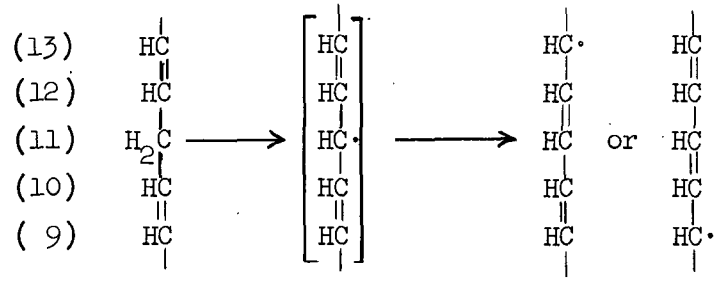


(24)

However, the above mechanism does not explain the autocatalysis of the oxidation or the formation of the monomer and dimer reaction products; apparently, these are explained better by a monoradical process involving the abstraction of a hydrogen from the eleostearate. Evidently the kinetic mechanisms are not as well elucidated for the secondary oxidation reactions as for the formation of the hydroperoxide.

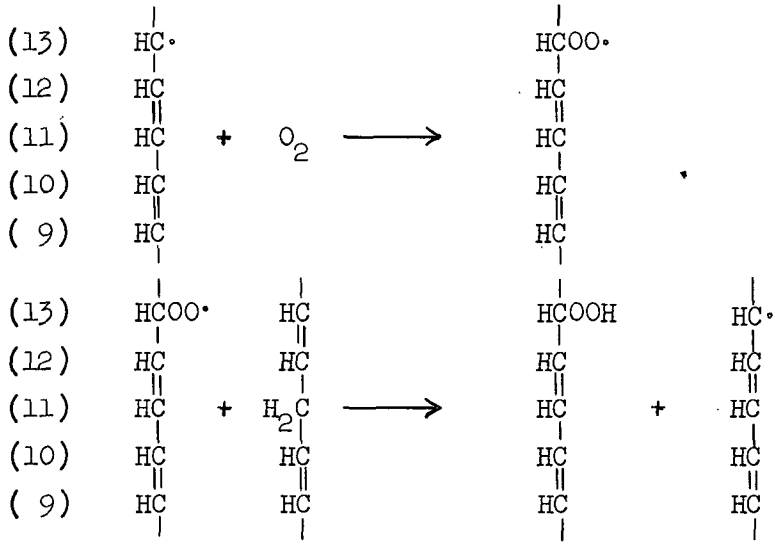
OXIDATION PRODUCTS FROM LINOLEIC ACID

The initial attack of the free radical on the linoleic acid is at the eleventh carbon atom which is accompanied by simultaneous conjugation of the double bond (67-71). The reaction is as shown in Equation (24) (only the reactive center of the hydrocarbon chain is shown):



(24)

Oxidation of the free radical produces either the 9 or 13-hydroperoxide of the linoleic acid, of which only the 13-hydroperoxide is shown.



(25)

(26)

The 11-hydroperoxide has not been isolated nor has evidence been obtained for its existence. There is a difference of 7 kilo-calories per mole between the conjugated and unconjugated states due to the spreading of the π electrons, and this could explain why the unconjugated hydroperoxide is not found. Both the cis-trans and trans-trans conjugated isomers are produced. However, the evidence indicates that the cis-trans isomer is formed initially and then isomerized to the trans-trans form.

The type of products formed during the production and breakdown of the hydroperoxide will depend upon the relative rates of the reactions (13-17). These will depend upon the temperature, oxygen partial pressure, and the reactivity and concentration of the linoleic acid. The effect of temperature is particularly important. For example, the reaction rate constants and the corresponding activation energies for the oxidation of tetralin at 25°C. are shown in Table II.

TABLE II

REACTION RATE CONSTANTS OF TETRALIN (54)

Reaction	Rate Constants, $(mole/l.)^{-1} sec.^{-1}$	Activation Energies, kilocalories
13	6.8×10^7	0.0
14	13.3	4.5
15	7.1×10^6	2.6
16	2.2×10^7	0.4

From the activation energies it is evident that higher temperatures will favor reactions (14) and (15). Thus, higher temperatures favor termination of unoxidized free radicals. The same consideration holds true for the linoleic acid. High temperatures and low oxygen partial pressure should favor a high concentration of carbon-to-carbon bonds in the reaction products. Conversely, low temperatures and high oxygen partial pressures should favor more oxygen to carbon linkages in the reaction products. These conclusions arrived at from kinetic data are confirmed to some extent through analysis of the oxidation products. Witting, et al., (72) pointed out that thermal polymers produced in the autoxidation of ethyl linoleate become progressively insoluble in oxygen-bearing solvents whereas low temperature autoxidative polymers become progressively insoluble in nonpolar solvents. Johnson, et al., (73) studied the decomposition of methyl linoleate hydroperoxide both in oxygen and nitrogen. As expected, the products resulting from decomposition

in the oxygen atmosphere were more polar than those produced by decomposition in a nitrogen atmosphere. However, Knight, et al., (74) autoxidized methyl oleate at 35, 70, and 100°C. and found that 2.5 to 3.0 atoms of oxygen were introduced per mole regardless of the temperatures. However, at higher temperatures more ether linkages are formed. Thus, high temperatures lead to less oxygen-to-carbon linkages except where the oxygen directly attacks the double bond, and decreasing the concentration of oxygen undoubtedly leads to less oxygen in the hydroperoxide decomposition products.

The breakdown of hydroperoxides and oxidation of the double bonds of linoleic acid result in a number of monomeric products (73-80). At room temperature, increases in carboxyl oxygen, ester oxygen, hydroxyl oxygen, oxirane oxygen and carbonyl oxygen are noted. Also, acids may be produced by scission of the double bond (65). Gaddis and Carrie (78) analyzed the steam volatile monocarbonyl compounds in mildly autoxidized linoleic acid ester and found the aldehydes which would be expected from scission of the hydrocarbon chain. Also, Vioque, et al., (77) oxidized ethyl linoleate with lipoxidase and found that the products contained the 9-keto-11, 13-octadecadienoate and the 13-keto-9, 11-octadecadienoate. Khan, et al., (75) obtained cis-trans and trans-trans conjugated hydroxy octadecadienoate upon autoxidation of methyl linoleate at -10°C. Significantly, the same product was obtained when the oxidation was carried out in the presence of a copper catalyst. The presence of water seems to favor the hydroxy acids. For example, Mabrouk, et al., (79) autoxidized linoleic acid in an aqueous solution and believed the major compound to be a tetrahydroxy compound whose exact structure was not determined. Schauenstein, et al., (80) also found that hydroxy acids were the main reaction products when oxidation was carried out in the presence of water. In summary, monomeric products produced upon decomposition of the hydroperoxide are what might be expected from scission of the double bond and loss of oxygen from or dehydration of the hydroperoxide.

The breakdown of the hydroperoxides and oxidation of the conjugated double bond can also lead to formation of covalent bonds between the linoleic acid molecules to form dimers and trimers (65, 72, 73, 81-86). At high temperatures the linoleic acid dimerizes by means of the Diels-Alder reaction or through the coupling of two free radicals (81). The older literature favored the Diels-Alder mechanism (82), but the more recent experimental evidence indicates that the free radical coupling mechanism may be more nearly correct. Williamson (83) found that thermal decomposition of methyl linoleate hydroperoxide produced dimers linked through a carbon-to-carbon bond. Those dimers which contained a large amount of the original unsaturation were not hydroxylated, but those which had lost a lot of the unsaturation were hydroxylated. Also, trimers were formed which probably consisted of two monomeric units linked through carbon-to-carbon bonds and the third through oxygen linkages. Rushman, et al., (84) also found that dimers, linked through carbon-to-carbon bonds, were formed during the thermal polymerization of methyl linoleate. Rushman, et al., postulated that a methyl linoleate molecule abstracts a hydrogen atom from a second linoleate molecule to form simultaneously two free radicals which then undergo a coupling reaction. Finally, Frankel, et al., (85) thermally decomposed the hydroperoxides of linoleate esters at 210°C. and found the principal reaction was dimerization of the fatty acid chains with elimination of the hydroperoxide groups. The experimental evidence indicated that a six-membered ring did not form as demanded by the Diels-Alder reaction, and thus the authors concluded that dimerization occurred through alkyl or alkoxy hydroperoxide radicals to produce carbon-to-carbon bonds. In summary, at high temperatures the linoleic acid may be expected to polymerize to form dimers or trimers through carbon-to-carbon linkages.

At low temperatures, dimers and trimers are also formed in the autoxidation process, but the bonds are mainly those in which carbon is linked to oxygen

(65, 72, 73, 86). Kummerow, et al., (65, 72, 86) in a series of papers studied the autoxidation of 9,12-linoleic acid and its methyl ester, and also the autoxidation of the conjugated 10,12-linoleic acid and its methyl ester over a temperature range of 30 to 100°C. The amount of oxygen uptake was equivalent to the amount of diene lost for the conjugated acid or ester at 30°C. This suggested that carbon-to-oxygen rather than carbon-to-carbon bonds were being formed. Initially, the rate of decrease of the conjugated double bonds was greater for the conjugated acid as compared with the unconjugated acid. However, after the maximum hydroperoxide concentration for the unconjugated acid was obtained, the rate at which conjugated diene decreased was approximately the same for both acids. The addition of metallic naphthenate driers to the acids increased the rate of diene conjugation of the unconjugated acid and promoted the destruction of conjugated diene for both the conjugated and nonconjugated acids. Thus, the net effect of adding the driers was to increase the rate of polymerization. The authors found that the polymers formed upon autoxidation of ethyl linoleate were depolymerized by 3.4N ethanolic HCl from an average initial molecular weight of 758 down to 296. Thus, they proposed that the monomers were linked through a dioxane ring or a peroxide bond. Johnston, et al., (73) analyzed the decomposition products from methyl linoleate hydroperoxide decomposed at 4°C. in darkness in both nitrogen and oxygen atmospheres. The products derived from the decomposition in oxygen were more polar than the original hydroperoxide and exhibited mainly an isolated trans-bond with only traces of the cis-trans conjugated material. This material also contained hydroxyl or hydroperoxide groups which were largely associated. The molecular weight was such that a considerable portion of the material consisted of dimers which lacked conjugated double bonds. The products formed when the decomposition of the hydroperoxide was carried out under nitrogen also showed a large loss in cis-trans conjugation. However, these reaction products were not as polar as when the decomposition was carried out in oxygen. A major portion of the material had a molecular weight

which would suggest that it was a dimer which lacked diene conjugation. Thus, at room temperature, polymeric material, dimers and trimers, can be formed by the breakdown of the hydroperoxides produced in the initial stages of oxidation and also by direct attack of oxygen at the conjugated double bonds. The formation of the low molecular weight polymers is accompanied by loss of the diene conjugation, and the acid molecules appear to be linked through oxygen-to-carbon bonds. These bonds may be either a dioxane or peroxy type of linkage.

In summary, the analysis of the products of autoxidation of linoleic acid and its esters confirm in principle the proposed kinetic theory. The initial point of attack is at the methylene hydrogen alpha to the double bonds to form a free radical. During this process the double bonds are conjugated. The free radical is subsequently oxidized to the peroxy radical which reacts with another acid molecule to form the hydroperoxide and a new free radical. The hydroperoxides break down by a bimolecular or unimolecular reaction to form new free radicals, dimers, and monomeric products some of which arise from scission of the double bond. Ultraviolet light, metallic ions, high temperatures, and oxygen catalyze the breakdown of the peroxides. Also, oxygen can attack the conjugated double bonds directly to form polymeric and monomeric products. Such attack usually results in a loss of diene conjugation. Generally, high temperatures and low oxygen partial pressures favor carbon-to-carbon linkages in the degradation products whereas low temperatures and high oxygen partial pressures result in oxygen-to-carbon linkages.

STATEMENT OF THE PROBLEM

It is evident that autoxidation of unsaturated fatty acids and their esters increases the cohesive forces between the molecules because of the formation of covalent bonds and because of the introduction of polar groups into the hydrocarbon

chain. Such reactions lead to the hardening of thick films of unsaturated fatty acids which are initially liquid. Thus, if the autoxidation of the linoleic acid monolayer is similar to the autoxidation of bulk phases, the contact angle between water and the monolayer could increase due to a decrease in the mobility of the oxidized molecules. However, there exists the possibility that the hydrophilic groups introduced during autoxidation may be present in the outermost surface of the monolayer, and therefore, a hydrophobic surface may not be formed even though the molecules are immobilized. Thus, the present study was undertaken so as to ascertain how autoxidation of a linoleic acid monolayer would affect the contact angle with water and methylene iodide. The objectives of the study were to relate changes in the contact angle to the chemical changes occurring during autoxidation and this in turn to the mobility of the oxidized molecules.

EXPERIMENTAL PROCEDURES

MEASUREMENT OF MONOLAYER PRESSURE-AREA ISOTHERMS

The pressure-area isotherms of the linoleic acid monolayers were measured with a Cenco Horizontal Hydrophile Balance which was similar to the film balance shown in Fig. 2 except for the absence of a well in front of the float. A detailed description of the operation of the film balance can be found in Appendix I. The monolayers were spread on an aqueous 0.01N HCl substrate from a hexane solution of unlabeled linoleic acid. This substrate was used in order to minimize the amount of salt formation in the monolayer by keeping the carboxyl group in the unionized state. Hexane was selected as the spreading solvent because of its high spreading pressure, high volatility, and low solubility in the substrate. Two concentrations of linoleic acid were used, 0.874×10^{-3} and 0.874×10^{-2} molar, in order to ascertain if the solute-to-solvent ratio had any effect on the isotherm. The temperature of the substrate was maintained at $22 \pm 0.5°C$.

The substrate surface was cleaned by sweeping with a movable barrier until no decrease in the surface tension was noted upon moving the barrier from the far end of the tray up to the float. A known volume of the linoleic acid solution was deposited onto the surface with a micropipet; three minutes were allowed for the hexane to evaporate. The amount of linoleic acid deposited was reproduced to within $\pm$ 2%. After the hexane had evaporated, the film was compressed and the torsion required to elminate deflection of the float and the distance from the barrier to the float were recorded. The pressure at constant area decreased with time due to solution of the linoleic acid in the substrate, evaporation of the acid from the surface and/or oxidation of the acid to fragments which were soluble in the substrate. This decrease in area necessitated measuring only half the isotherm at one time. About four minutes were required to measure half of the isotherm.

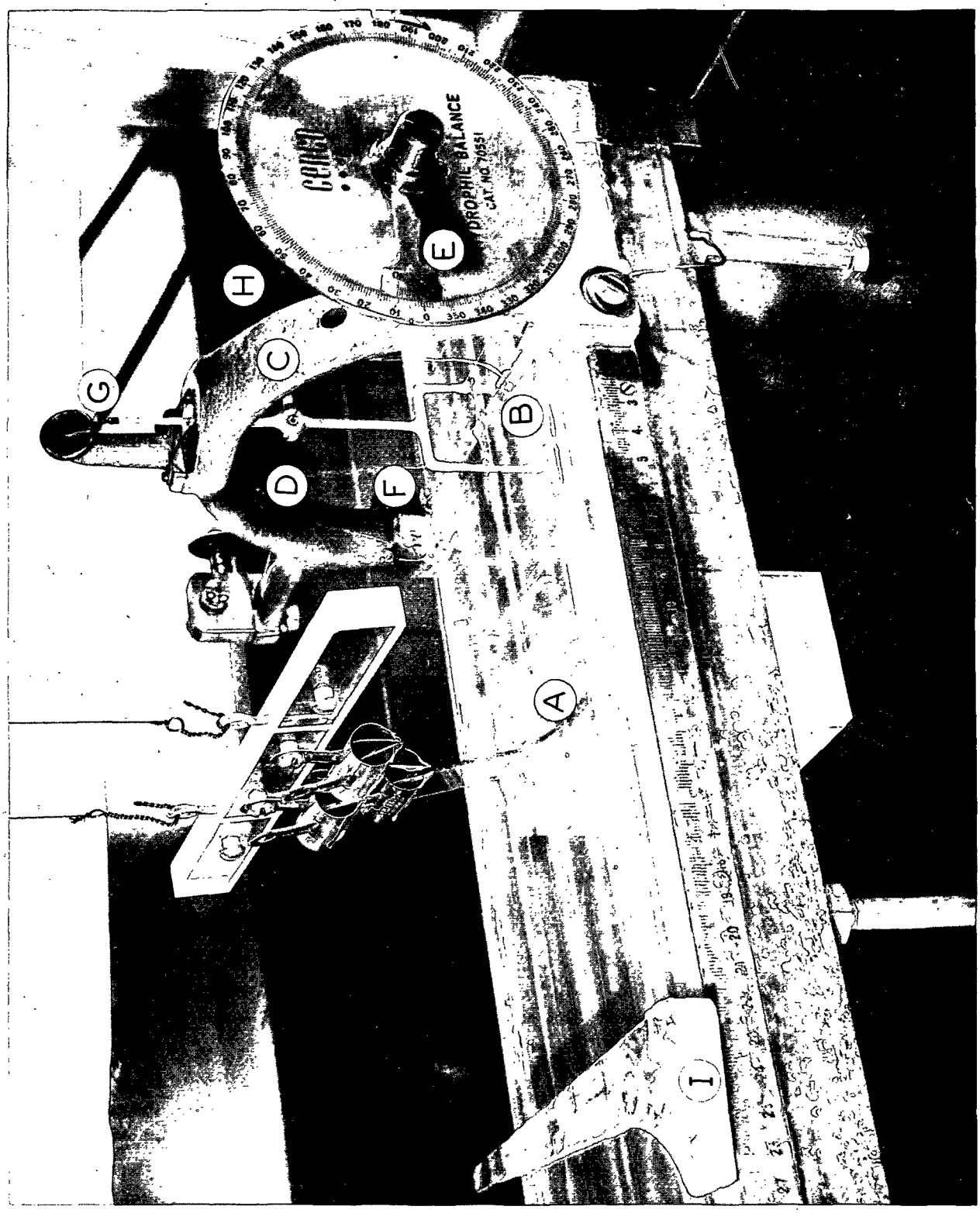


Figure 2. Horizontal Film Balance

Three complete isotherms were determined for each concentration of linoleic acid. Data on oleic acid isotherms were also obtained under the same conditions and compared to data in the literature in order to ascertain if the experimental techniques were suitable.

FORMATION OF MONOLAYERS ON SOLID SURFACES

The formation of monolayers by adsorption from organic and aqueous solutions of linoleic acid was unsuccessful. Thus, monolayers were formed on an aqueous substrate and then transferred to the solid surface. The transfer was accomplished using the technique of Blodgett (87), which was modified by using a film balance to maintain the desired film pressure during transfer instead of a piston oil.

The surface of the .01N HCl substrate was cleaned by sweeping as described previously. When the surface was cleaned of surface-active impurities, glass slides were lowered through the substrate surface into the well in front of the float as shown in Fig. 2. A 1-C^{14} labeled linoleic acid monolayer was spread from approximately a 10^{-3}M hexane solution, as previously described, and four minutes were allowed for the hexane to evaporate. The monolayer was then compressed to the desired film pressure. The film pressure was set so as to effect the most compact monolayer on the slide surface. Once at the desired film pressure the glass slide was slowly raised through the substrate surface. At the same time, the barrier was moved towards the float at a rate sufficient to maintain the film pressure constant. The monolayer was formed and transferred at 22 $\pm$ 0.5°C.

All of the operations were performed under a dust shield which covered the trough completely. The slide was raised by means of an electric motor connected through a gear reduction drive to a pulley system by means of a belt. The pulley was mounted on the wooden frame of the dust shield. The glass slides were held

in teflon-covered paper clips which were attached to a plastic bar, which was then suspended from the pulley system by means of silk threads.

The rate at which the slide was raised through the surface did not materially affect the amount of acid transferred as shown by analysis of the radioactivity of the monolayer (see Table III). Thus, all monolayers were transferred with the slide moving through the surface at 1.5 cm. per minute.

TABLE III

EFFECT OF RATE OF DEPOSITION UPON THE AMOUNT DEPOSITED

Monolayer No.	Rate of Deposition, cm./min.	Count, c.p.m.
9-1	1.5	1,201
9-2	1.5	1,208
9-3	1.7	1,227
9-5	2.0	1,194
9-4	2.8	1,232

Monolayers were also formed and transferred to the solid surfaces in a nitrogen atmosphere which contained less than 0.1% oxygen. The slides were then sealed in containers to age while still under nitrogen so that the oxygen concentration was kept very low. The procedure for forming and transferring the monolayers in the nitrogen atmosphere was the same as in air except that the slides were raised through the substrate surface by manual manipulation of a pulley system. However, the temperature control was not as precise, being approximately $23 \pm 3°C$.

The monolayers were transferred to two types of solid surfaces: 3 by 1-inch glass microscope slides and polished copper plates of the same dimensions. The glass microscope slides were used because they are quite smooth (88), easy to

clean and the carboxyl group of the fatty acid did not react with the surface as shown in Table IV.

TABLE IV

SOLUBILITY IN HEXANE OF A STEARIC ACID MONOLAYER ON A GLASS SURFACE

Monolayer No.	Time of Aging, hours	Monolayer Soluble in Hexane, %
21-1	0.0	98.1
21-2	20.8	95.4
21-3	42.8	93.8
21-4	66.8	95.4
21-5	113.2	93.8

The copper plates were used because the carboxyl group of the fatty acid reacts with the copper as shown in Table V and as found by other authors (89-91).

TABLE V

SOLUBILITY IN HEXANE OF A LINOLEIC ACID MONOLAYER ON A COPPER SURFACE

Monolayer No.	Time of Aging, hours	Monolayer Soluble in Hexane, %
74-1	0.0	25.1
74-2	5.5	14.8
74-3	18.2	6.6
75-1	45.3	4.4
75-2	96.3	1.3
75-3	138.7	0.4

The copper plates were not as smooth as the glass slides. However, the evaporation of copper onto glass slides to form a very smooth copper surface was unsatisfactory. Apparently, the dilute hydrochloric acid solution attacked the copper which

destroyed the bond between the copper and the glass. This resulted in a peeling of the copper film from the glass surface during transfer of the monolayer.

The reproducibility of the concentration of linoleic acid on the surface, as determined by assay of the monolayer radioactivity, was ± 2% (95% confidence limit) for the glass and ± 23% (95% confidence limits) for the copper (see Tables VI and VII). The reasons for the decrease in the reproducibility on the copper surface will be discussed later. However, for the monolayers on copper which were analyzed with regard to the contact angle with water and methylene iodide, the concentration was maintained within ± 15%. These limits on the reproducibility of the acid concentration include all of the scatter introduced by variations in the solid surfaces, in the aqueous substrates, and in the various factors involved in assaying the radioactivity of the monolayer.

ANALYSIS OF THE CONCENTRATION OF THE LINOLEIC ACID ON THE SURFACE

Analysis of the linoleic acid concentration in the monolayer was based upon the assay of the radioactivity of the 1-C^{14} labeled portion of the linoleic acid. It was assumed that the labeled acid behaved the same as the unlabeled acid during the formation of the monolayer and also during autoxidation.

It is unlikely that the labeled acid behaved differently than the unlabeled in either of these processes. The acid was labeled specifically in the one position (carboxyl group) which represents only about 4.3% of the total weight of the molecule. The difference in the rate of movement between a C^{14} and C^{12} atom due to the difference in the mass is probably about 7% (92). Thus, the effect of the C^{14} atom on the rate of movement of the total molecule would probably be very small. In addition, the transfer of the monolayer from the aqueous to the solid surface was almost an equilibrium process and little movement of the molecules occurred.

TABLE VI

REPRODUCIBILITY OF MONOLAYER DEPOSITION ONTO GLASS[a]

Monolayer No.	Count, c.p.m.
16-1	1,208
16-2	1,216
17-5	1,198
17-6	1,209
18-5	1,217
18-6	1,197
19-1	1,218
19-2	1,210
19-3	1,211
19-4	1,239
19-5	1,225
Mean	1,213
Std. dev.	11.8

[a]Deposition pressure: 26.0 dynes per cm.

TABLE VII

REPRODUCIBILITY OF MONOLAYER DEPOSITION ONTO COPPER[a]

Monolayer No.	Count, c.p.m.
74-1	1,294
74-2	1,266
74-3	1,335
75-1	1,151
75-2	1,309
75-3	1,456
81-1	1,182
81-2	1,124
Mean	1,265
Std. dev.	108.5

[a]Deposition pressure: 13.0 dynes per cm.

Presumably, the labeled acid autoxidized no differently from the unlabeled acid, because of the large distance between the labeled carboxyl group and the site of the oxidation reactions which occur between the 9 and 13 carbon atoms. However, chromatographic analysis of the labeled acid showed that about 3.86% neutral material was present. This neutral material may not oxidize or form a monolayer in the same way as does the linoleic acid and probably introduces the principal error in the radioactive analysis with regard to differences in behavior of the labeled and unlabeled material.

IONIZATION GAS FLOW COUNTER

An ionization gas flow counter was used to measure the radioactivity of the monolayers. The instruments were manufactured by Nuclear Chicago Corporation and

consisted of a Model D-47 Gas Flow Detector equipped with a preamplifier whose output was fed into a Model 182 Scaler. The detector works on the ionization principle and can be used in both the Geiger and proportional regions. The ionization chamber is continuously flushed with the ionizing gas. The detector was used in the proportional region with the window in place over the front of the ionization chamber. The counting gas was Nuclear-Chicago's "PR Gas" which is 90% argon and 10% methane and the pressure between the regulating capillary and the tank was maintained at 7 p.s.i.g. The millivolt and threshold controls of the scaler were set at one, so that the sensitivity of the instrument to pulses from the counter was one millivolt. The high voltage was set at 1,950 volts which was approximately in the center of the plateau region. The preamplifier was set at unit sensitivity.

A counting procedure was developed whereby a quantitative comparison between the radioactivity of monolayers was obtained. The factors involved in the counting efficiency of the detector which must be controlled to obtain quantitative data are as follows (93):

(1) Absorption by the window over the ionization chamber;

(2) Absorption by any material between the monolayer and the sample;

(3) Self absorption of the monolayers;

(4) Backscattering of the substrate;

(5) Geometric relationship between the monolayer and the ionization chamber.

The absorption properties of the windows used to cover the ionization chamber were sufficiently uniform so as not to materially affect the counting efficiency when changed. The self absorption of the monolayer was negligible and the backscattering was constant for a given substrate. The geometry of the system was

kept constant by constructing a holder, A, which positioned the slide, B, under the ionization chamber, D, in the same location each time (see Fig. 3). In addition, the monolayer was always deposited over the same area of the glass slide so that its position relative to the ionization chamber was kept constant.

However, it was necessary to place a replaceable plastic film, C, over the end of the adapter to prevent contamination of the detector due to evaporation of the linoleic acid from the monolayer. Commercial "Handiwrap" was placed over the adapter with a rubber band and holes were punched into the wrap to allow the counting gas to escape. The weight per unit area was sufficiently uniform so that the film could be changed without the introduction of a large analytical error. Attempts to calibrate the plastic film with a standard beta source were unsuccessful. The calibration procedure introduced more errors into the results instead of eliminating them. When analyzing the reproducibility of depositing monolayers onto glass, it was found that the results varied $\pm$ 2% at the 95% confidence limits. This included the scatter introduced by different glass substrates, different aqueous substrates, different windows over the ionization chamber, and different plastic films over the adapter. When the film was calibrated and the data corrected accordingly, the scatter was $\pm$ 4.7%. Since the error in analyzing the radioactive count without calibration of the film was almost within the expected error, the film was not calibrated. Thus, all of the factors which affect the counting efficiency of the detector (other than instrument design) were controlled, permitting a quantitative comparison of the amount of material on the surfaces.

The rate of emission of electrons from a beta source varies with time and the distribution can be approximated by a Poisson curve. Thus, the accuracy of the analysis depends upon the total number of counts taken. A sufficiently large number of counts was recorded so that after correction for the background count,

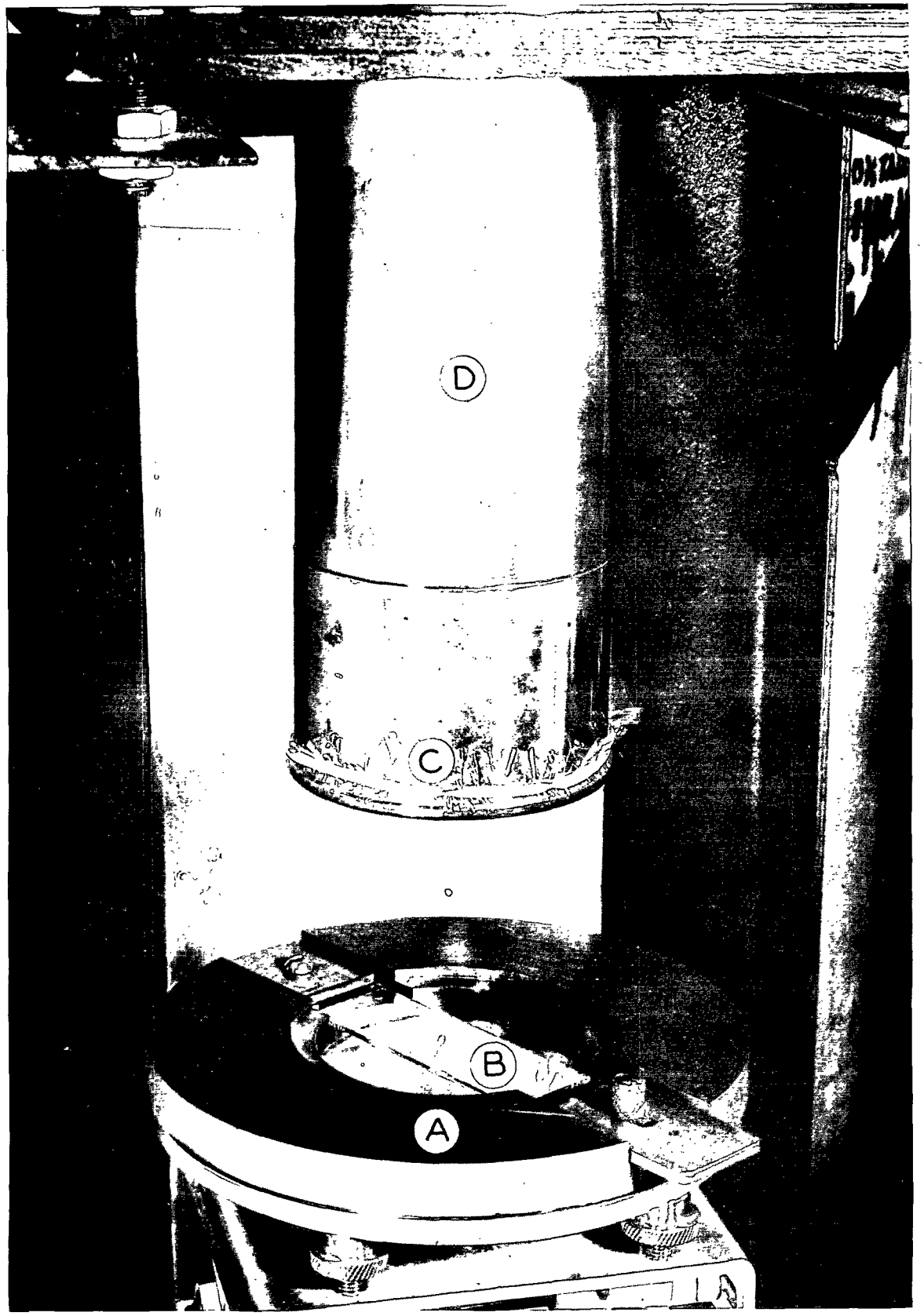


Figure 3. Gas Flow Counter

the counting error was within ± 1.96% for a monolayer and ± 3.6% for any concentration less than a monolayer using 95% confidence limits. The counting rate, about 1200 c.p.m., was not sufficiently high to require a coincidence correction.

AUTORADIOGRAPHY

Autoradiography was used to ascertain if there were any variations in the concentration of the linoleic acid on the slide surface due to the method of forming the monolayer. Also, it was used to determine the extent to which the monolayer spread upon the surface of the drop of water. Kodak film plates, Type A, were employed which had the same dimensions as the glass slides and which had a 0.5 μ protective coating over the emulsion. The glass slide containing the monolayer was prepared by wrapping a thin strip of masking tape around each end in order to prevent the film plates from coming into direct contact with the monolayer. This prevented damage to the photographic emulsion and also decreased the amount of linoleic acid transferred to the plate. The emulsion was exposed by sandwiching the glass slide containing the monolayer between two plates and then wrapping all three in aluminum foil to exclude any light. The three were held in place with a rubber band and then sealed in an envelope. Exposure was carried out at 22 ± 0.5°C. After sufficient exposure, the plates were developed in Kodak D-19 developer for five minutes and then fixed for eleven minutes in a hypo-bath. A constant rate of agitation was maintained throughout the developing procedure. The plates were then washed for 20 minutes and dried. The optical density of the developed film plates was measured with an instrument developed by Jentzen (94). The instrument was set at 100% transmission over that part of the film plate which was not exposed. The optical density of the exposed part of the plate was then read directly. The relationship between optical density and the product of the electron flux and the time of exposure was not linear due to failure of the reciprocity law (95). However, the data did fit the following equation (see Fig. 4):

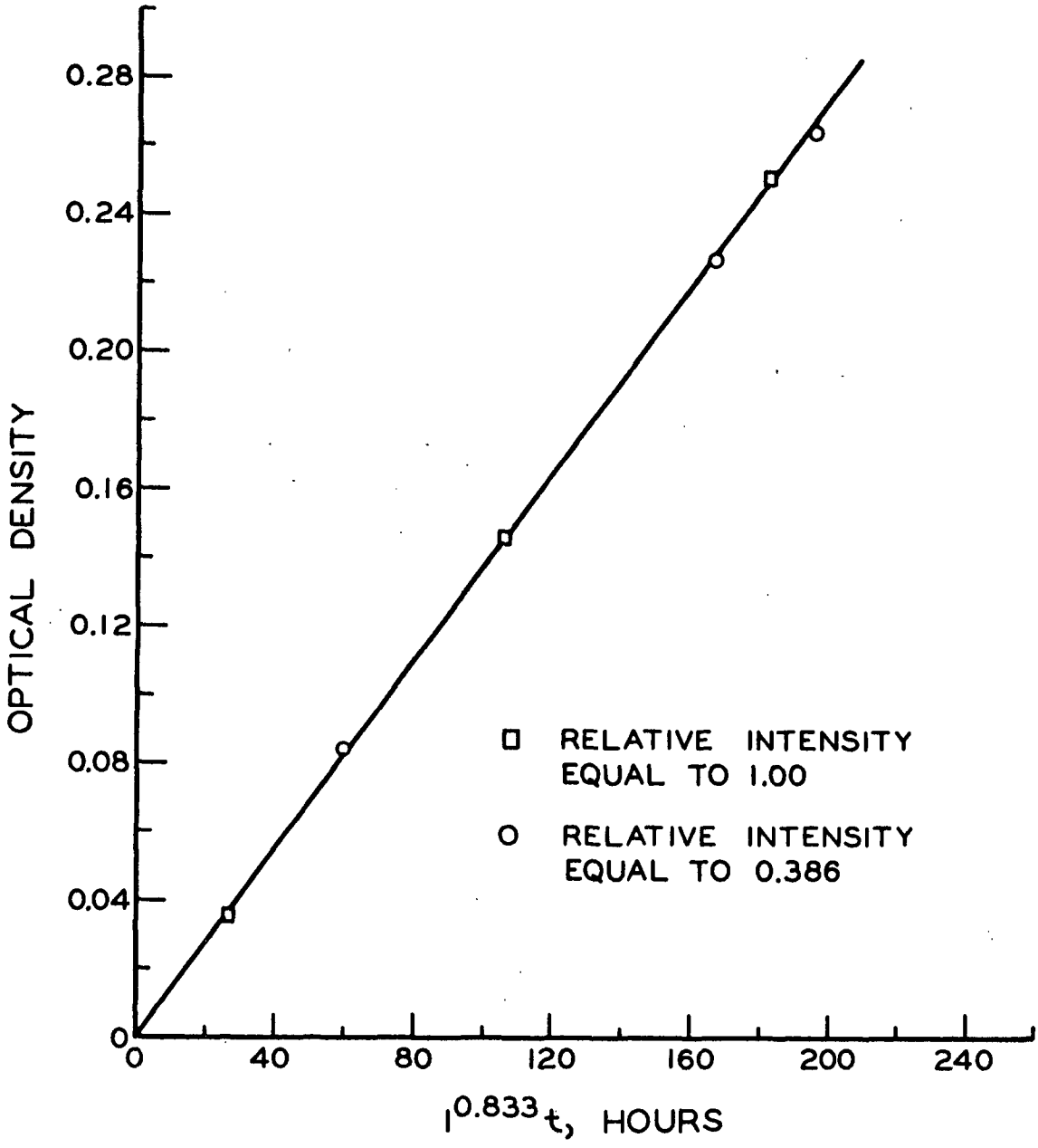


Figure 4. Relationship Between the Optical Density of the Film Plate and the Amount of Exposure to the Radioactive Monolayer

$$\text{Optical Density} = D = kI^{a}t \qquad (27)$$

$$D = .00138I^{0.833}t$$

where

$\underline{I}$ = the relative intensity of the electron flux;

$\underline{t}$ = the time.

The relative intensity was determined from the count of the monolayers. The count obtained with the most compact monolayer formed from the labeled acid having the highest specific activity was set equal to one. The count obtained on any other monolayer was then compared with this maximum count so as to determine the relative intensity. From Equation (27) variations in the concentration of the acid on the surface were calculated. Since the intensity of the electron flux is equal to the molar surface concentration of the linoleic acid for a given specific activity, the relative concentration of the linoleic acid over the slide surface could be calculated from the optical density.

AGING OF THE MONOLAYERS

The monolayers were aged in air and nitrogen at 25 $\pm$ 0.05°C. in the absence of light and in both the absence and presence of water vapor.

The slide containing the monolayer was suspended from the cover of a 16-ounce bottle by means of paper clips covered with teflon tape, and the bottle was weighted by lead shot which was then covered with paraffin. The cover was sealed first by wrapping plastic electrician's tape around the outside and then applying melted paraffin over the tape. Light was excluded by wrapping the bottle in aluminum foil. The bottle was then submerged in a constant temperature bath maintained at 25 $\pm$ 0.05°C.

The concentration of water vapor in the atmosphere was controlled by placing either anhydrous calcium sulfate (drierite) or a saturated solution of calcium nitrate in the bottom of the bottle. The saturated solution of calcium nitrate produced an atmosphere of 50% relative humidity at 25°C. (96), and the relative humidity over the drierite was essentially zero.

The concentration of oxygen in the air atmosphere was approximately 20% (partial pressure 152 mm. of mercury), and the concentration in the nitrogen atmosphere was less than 0.1% (partial pressure less than 0.760 mm. of mercury). Because the bottles were sealed during oxidation, there was a continual loss of oxygen from the atmosphere as oxidation progressed. However, the oxygen was in sufficient excess so that the loss had a negligible effect on the reaction. The molar ratio of oxygen to linoleic acid in the air was about 2×10^5 to 1 and in the nitrogen atmosphere about 200 to 1. The rate of oxidation when carried out in nitrogen should decrease, but the maximum amount of oxidation should be the same because there was still a large excess of oxygen present in the atmosphere.

DETERMINATION OF THE DEGREE OF AUTOXIDATION OF THE MONOLAYER

Two methods were used to determine the amount of the monolayer which was autoxidized. The oxidized molecules were separated from the unoxidized by the difference in their solubility in hexane, and also through the use of reverse-phase chromatography. These techniques did not give information relative to the extent of oxidation of the acid, but analysis of the functional groups did furnish some of this information.

SOLUBILITY OF THE MONOLAYER IN HEXANE

The glass slide containing the monolayer was immersed in 200 ml. of purified hexane and held motionless for a period of four minutes. The hexane was kept dry with drierite and the temperature maintained at 25 ± 0.05°C. Drying was essential so as to obtain reproducible results. At the end of four minutes the slide was withdrawn carefully, residual solvent allowed to evaporate at room temperature, and the radioactivity determined.

The separation of the unoxidized material from the oxidized should be fairly quantitative since the oxidized long-chain fatty acids are usually quite insoluble in hexane (97). The soluble portion of the monolayer was mostly removed within the first 30 seconds of immersion and after four minutes there was essentially no further removal of this material (see Fig. 5). This indicates that a fairly clean separation of the two components was obtained. Analysis of the hexane-insoluble material at various levels of oxidation with reverse-phase chromatography indicated that this insoluble material was about 90% oxidized when the monolayers were aged in the absence of water vapor (see Table VIII). The separation was not as sharp for the monolayers aged in the presence of moisture, and a considerable amount of unoxidized linoleic acid was also retained in the monolayer. The possible reasons for the retention will be discussed later. However, the separation was complete enough when aging was done in dry air so that the amount of the monolayer insoluble in hexane was a reasonable measure of the amount of autoxidation. The amount of autoxidation was calculated from the ratio of the count per minute after immersion* over the count per minute before immersion.

* The count per minute after immersion was corrected for the 10% unoxidized linoleic acid which remained after immersion in the hexane.

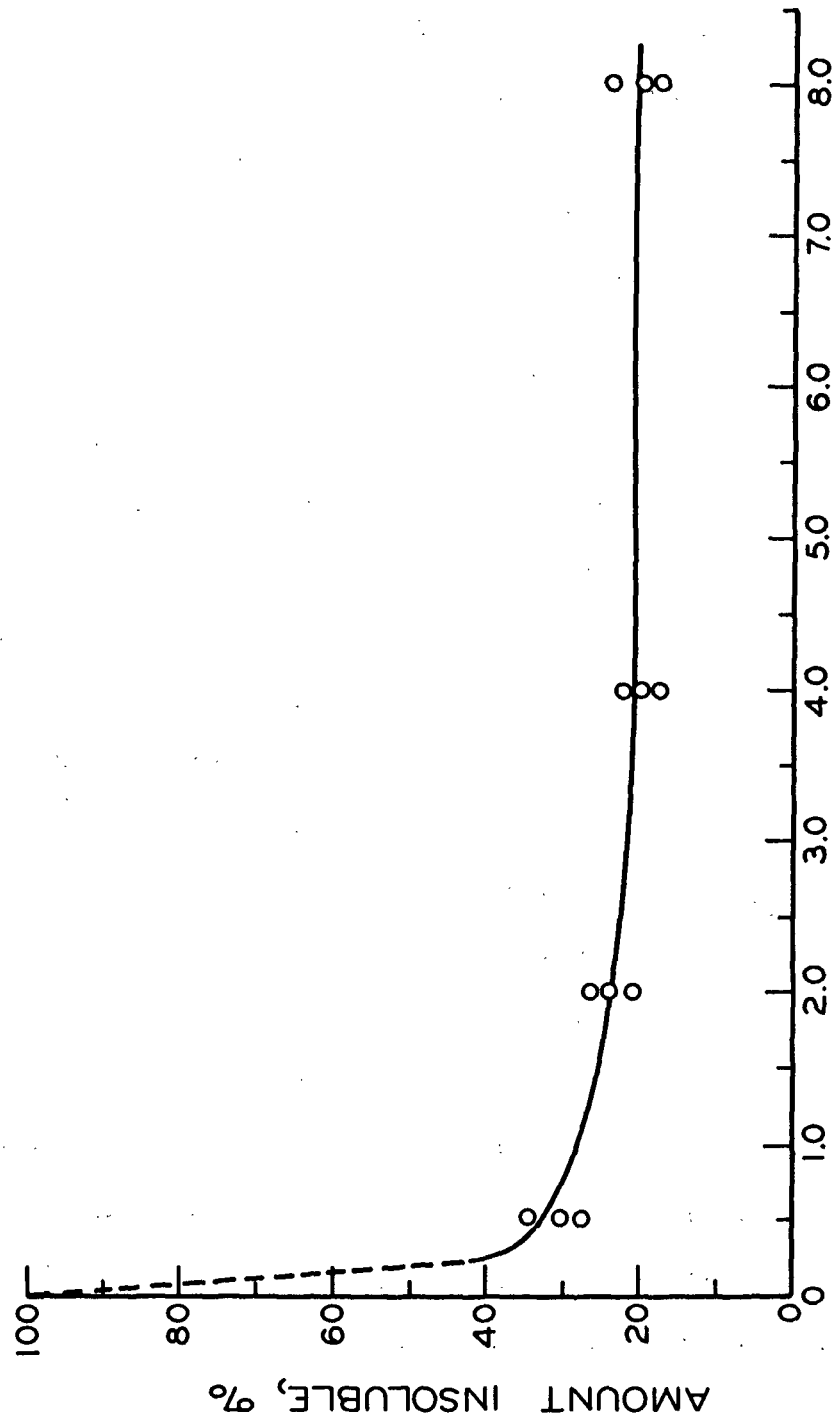


Figure 5. Amount of Monolayer Insoluble in Hexane as a Function of the Time of Immersion

TABLE VIII

CHROMATOGRAPHIC ANALYSIS OF HEXANE-INSOLUBLE MATERIAL

Monolayer No.	Time Of Aging In Air, hours	Hexane-Insoluble Material Oxidation, %
49-1 49-2	0.0	88.7
53-3 54-4	0.0	92.4
79-2	17.8	87.7
55-1 55-2	144.0	90.8
90-4	218.5	52.9[a]

[a]Monolayer number 90-4 was aged in the atmosphere of 50% relative humidity. The other monolayers were aged over drierite.

ANALYSIS OF THE MONOLAYER BY CHROMATOGRAPHY

Reverse-phase chromatography was used to analyze the monolayer as the oxidation progressed. The procedure of Schlenk, et al., (98) for analyzing relatively large amounts of fatty acids was altered so that the small amounts of material present in a monolayer could be determined.

The chromatographic paper, Whatman No. 1, was impregnated with mineral oil which had been washed with water to remove any oxidized material. The paper was impregnated by passing it slowly through an ether solution of the mineral oil, 7 grams of mineral oil per 100 ml. of ether, and then allowing the ether to evaporate. The developer was acetic acid and water in a ratio of 4:1. The mineral oil acts as the nonpolar phase and the developer as the polar phase. Thus, the oxidized or oxygenated fatty acids have high R_f values, and the unoxygenated acids low R_f values. The temperature was about 25°C. throughout most of the analysis. When analyzing

solutions of linoleic acid, the acid was spotted on the unimpregnated portion of the sheet in the normal manner and the unimpregnated end placed in the developer. When analyzing the linoleic acid monolayers, a one-inch wide strip of paper was impregnated to within five and one half inches from the end. The slide containing the monolayer was placed against the unimpregnated part, with one clean slide under the strip and another on top of the slide containing the monolayer. The three were clamped in place as shown in Fig. 6. The unimpregnated end was placed in the developer. As the developer moved through the paper by capillary action, it removed the oxidized and unoxidized linoleic acid from the slide and moved the material without separation until the impregnated section was reached. About 45 minutes was required for the solvent front to pass the length of the slide and remove the monolayer material. It is unlikely that a significant amount of the linoleic acid is autoxidized during this time (98). Chromatographic separation of the components started when they reached the impregnated portion of the sheet. About 18 hours were required for adequate separation.

The concentration of material in the various spots was determined through an analysis of the radioactivity of the spots. In this case a plastic shield was not placed over the adapter. The inch strip was centered under the window until the maximum count was obtained. The area of the spot affects the counting efficiency because of geometric considerations. However, because of the small amount of material analyzed, the area of the spots was comparable to or less than the area of the window. The difference in efficiency between a point source and an extended source which covers 0.75 of the area of the window is about 3% (99). Thus, the size of the spots does not introduce a large error into the calculations when the spot is smaller than the window of the counter.

C^{14} linoleic acid was spotted on chromatographic paper and allowed to oxidize for varying lengths of time prior to developing. Analysis of the linoleic acid

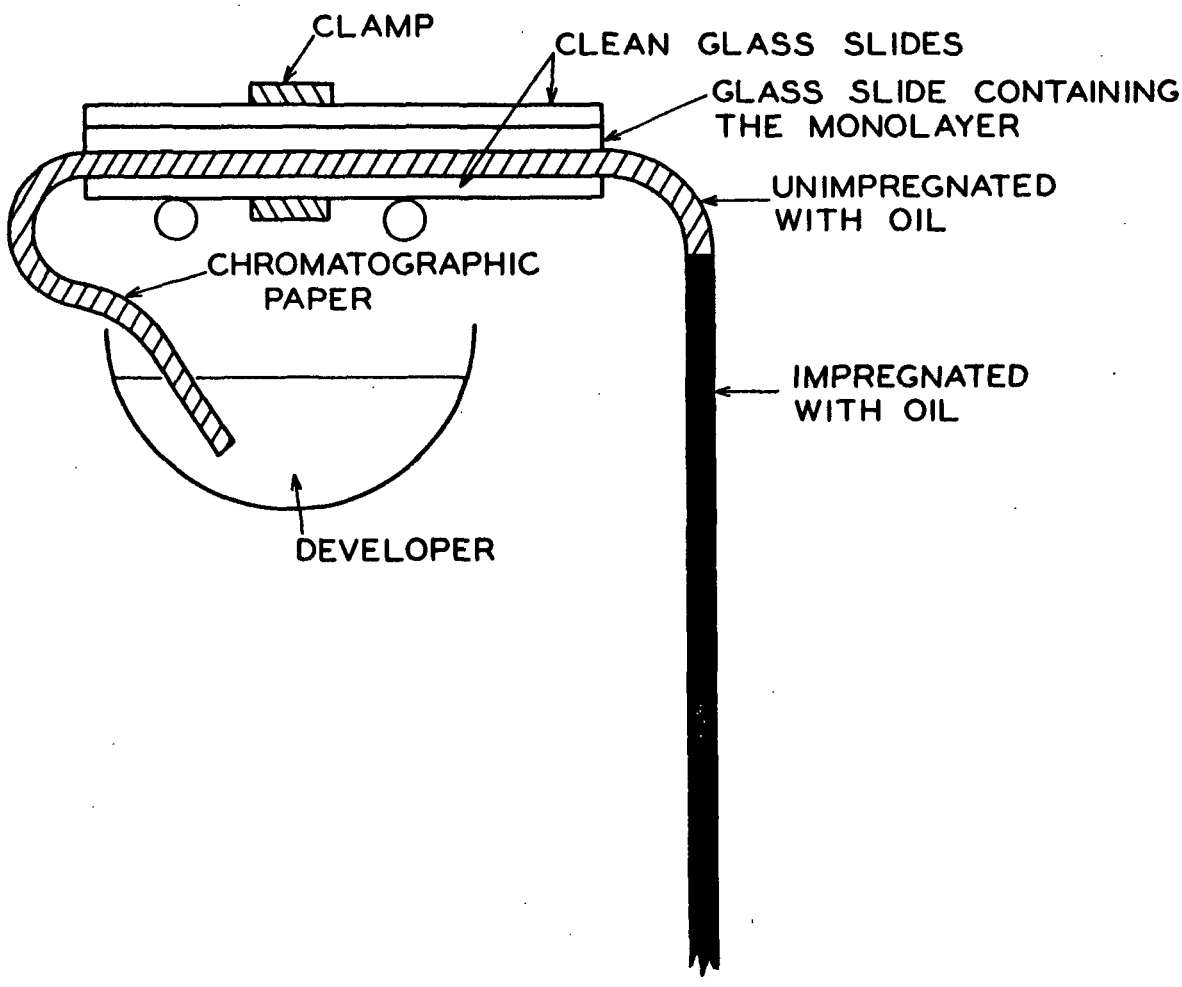


Figure 6. Chromatographic Technique for Analyzing the Autoxidized Monolayer

after oxidation is shown in Table IX. A build-up of material occurred at the base line and the solvent front which was accompanied by a decrease in the linoleic acid which moved with an R_f value of about 0.50. The material which moved at about R_f 0.25 was a neutral impurity contained only in the labeled portion of the linoleic acid (extraction of the solution with sodium hydroxide did not remove this material). This impurity amounted to about 0.2% of the total monolayer and should have a negligible effect on the oxidation reactions. The material at the base line and solvent front was considered oxidized linoleic acid and the data agreed with the findings of Schlenk, et al., (98). The material at the solvent front was highly oxygenated products, and the material at the base line was probably higher molecular weight material resulting from condensation reactions occurring during oxidation. Oxidation of the linoleic acid occurred in solution as shown by analysis at zero time of aging. However, the presence of oxidized linoleic acid in the spreading solution evidently does not affect the properties of the monolayer. This will be discussed later.

The per cent oxidation of the monolayer was calculated from the ratio of the sum of the counts of the material at the solvent front and base line over the sum of the counts of the solvent front, base line and the linoleic acid. At high degrees of oxidation, up to about 16% of the monolayer remained on the slide. This material was considered oxidized linoleic acid and the count of the chromatogram corrected accordingly.

ANALYSIS OF FUNCTIONAL GROUPS INTRODUCED INTO THE LINOLEIC ACID DURING AUTOXIDATION

Reductive polarography and ultraviolet (U.V.) absorption were used to analyze the oxidized linoleic acid. The difficulty in both analyses was to obtain enough material in a period of time so short that additional oxidation did not occur

TABLE IX

CHROMATOGRAPHIC ANALYSIS OF C^{14} LINOLEIC ACID AFTER OXIDATION

Time of Aging, hours	Spot No.	R_f Value	Total Count, %
0	Base line	--	0.605
0	Base line	--	0.720
24	Base line	--	2.32
48	Base line	--	4.44
0	1	0.242	3.61
0	1	0.256	3.57
24	1	0.242	3.18
48	1	0.256	3.85
0	2	0.499	80.5
0	2	0.525	85.0
24	2	0.499	70.2
48	2	0.525	59.6
0	3	0.915	16.2
0	3	0.869	10.9
24	3	0.915	24.4
48	3	0.869	32.4

during the isolation procedure. The amount of oxidized material needed for either polarography or U.V. analysis was quite small, being of the order of 8 μg.

ANALYSIS BY POLAROGRAPHY

A Sargent Model XII polarograph was used in analyzing the solution of oxidized linoleic acid. The current-voltage curve was measured with a Sargent Recorder, Model S-72150, connected in series with the polarograph which greatly increased the versatility of the instrument. The dropping mercury electrode assembly was as shown in Fig. 7. The cell was a conventional H cell, and a saturated calomel electrode was used as the reference electrode. The mercury pool was the cathode and the calomel electrode the anode. Prepurified nitrogen saturated with the solvent was used to deaerate the supporting electrolyte.* The drop time was 2.0 seconds, and the supporting electrolyte was 0.3M lithium chloride in a 50:50 mixture of reagent-grade methanol and benzene. The analysis was carried out at room temperature.

The polarogram (current-voltage curve) of the hexane-insoluble material was determined as follows:

(1) The hexane-insoluble material from five to six monolayers was isolated in a small amount of the supporting electrolyte.

(2) The supporting electrolyte containing the oxidized linoleic acid was placed in the cell and the total volume adjusted to 2 ml.

(3) The solution was deaerated and the dropping mercury electrode (cathode) placed below the surface of the supporting electrolyte.

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*The concentration of oxygen in the supporting electrolyte which was in equilibrium with the prepurified nitrogen was detectable polarographically. To remove the last traces of oxygen, a small amount of mercury was left in the bottom of the cell during deaeration.

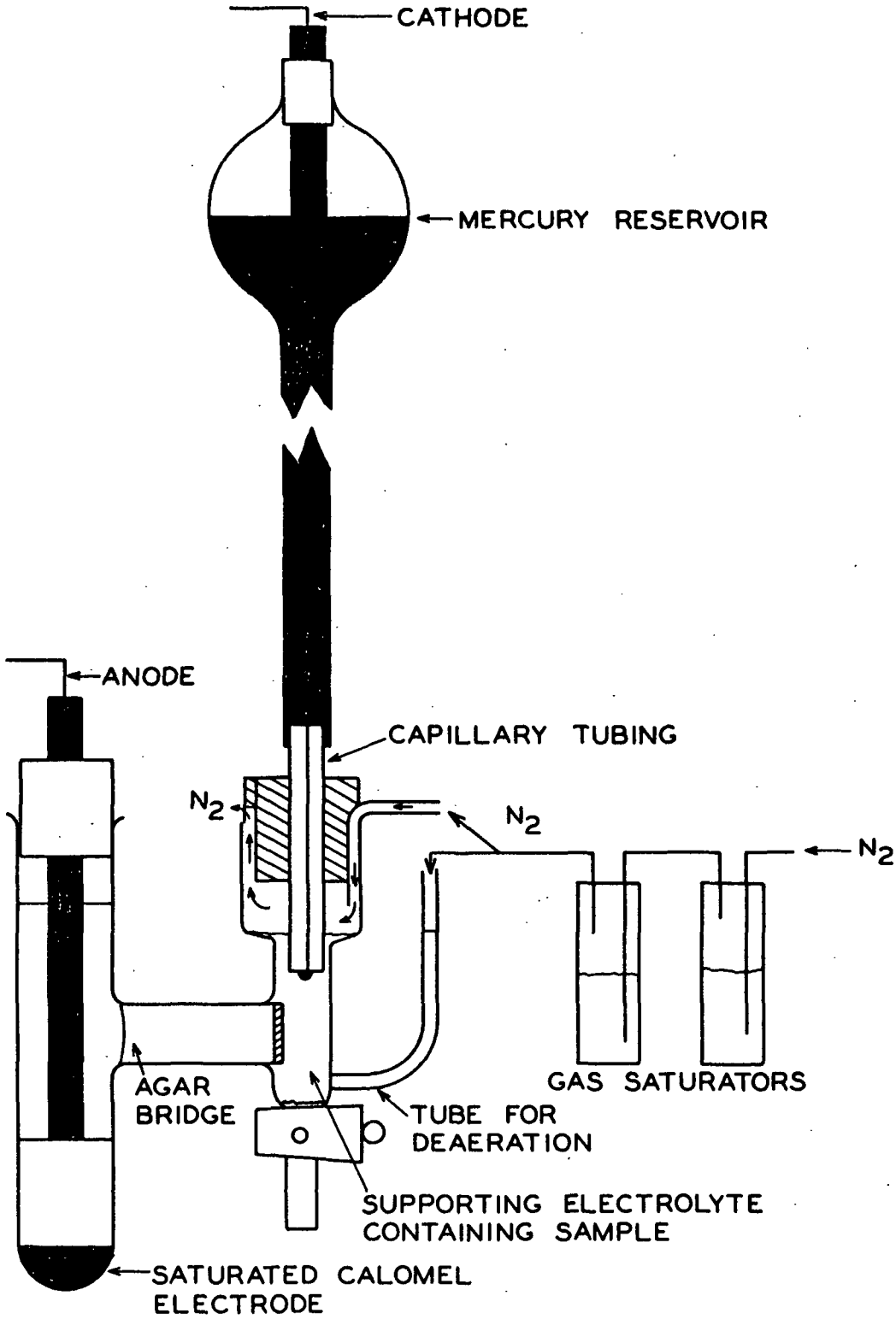

Figure 7. Dropping Mercury Electrode Assembly

(4) The current-voltage curve was measured over a voltage range from zero to minus two volts.

(5) The half-wave potentials of the reductive waves were determined after correcting for the residual current. The wave heights were not analyzed quantitatively because the concentration of the hexane-insoluble material could not be controlled accurately enough to warrant a quantitative estimate.

The main difficulty in the analysis was the isolation of the hexane-insoluble portion of the monolayer. Two methods were used. In the first method the material was removed with acetic acid in water, 4:1, by allowing the solvent to migrate in a strip of chromatographic paper placed against the monolayer much in the same manner as in the chromatographic procedure. As the solvent passed over the monolayer, it removed the hexane-insoluble material and concentrated it at the end of the strip, which was cut off and the material extracted with the supporting electrolyte after the acetic acid and water had evaporated. This method was not entirely suitable because small amounts of reducible sugars prevented analysis at voltages more negative than -1.5 volts. Glass mats were tried but they also contained a reducible component that was extracted by the supporting electrolyte.

The second method involved washing the hexane insoluble material from the slides with about 1.5 ml. of the supporting electrolyte. As oxidation in the dry atmosphere became more extensive, it was necessary to abrade the slide surface with a stainless steel spatula in order to remove the material. The material formed by oxidation in the presence of moisture was always readily soluble in the supporting electrolyte. This second method of isolation was more suitable than the former because the residual current was low enough to permit analysis of the diffusion current to -1.8 volts.

The uncertainty in the concentration of the oxidized material precluded quantitative analysis of the height of the diffusion current. Hence, the temperature was not controlled more closely during the procedure. However, analysis of the half-wave potentials permitted identification of reducible oxygen groups introduced into the linoleic acid by comparison with the half-wave potentials of oxidized fats and other compounds. The curves were analyzed by the techniques set forth by Meites (100). The average of the current fluctuations caused by the dropping electrode was taken as the proper value of the current at any particular voltage.

ANALYSIS BY U.V. ABSORPTION

An analysis of the U.V. absorption spectra of the monolayer material was made with the Beckman D.U. Spectrophotometer. Purified reagent-grade methanol and methanol containing 10% potassium hydroxide were used as solvents. Five or six monolayers were isolated by washing the slides with about 2 ml. of methanol as when isolating material for analysis by polarography. For the U.V. analysis both the oxidized and unoxidized material were isolated together because during the separation of the two components with hexane, benzene (present in the hexane in trace amounts) was adsorbed on the slide in amounts sufficient to contaminate the methanol. This occurred even though the benzene was in such trace amounts that it could not be detected from the U.V. spectrum of the hexane.

The U.V. spectrum was first run in neutral methanol. Then half of the methanol was evaporated and an equal volume of methanol containing 20% potassium hydroxide was added to produce a solution of 10% potassium hydroxide. The U.V. spectra were again determined in the alkaline methanol.

ANALYSIS OF THE CONTACT ANGLE

The contact angle between a sessile drop of water or methylene iodide and the monolayer was measured directly with a goniometer (see Fig. 8).

The goniometer consisted of a hairline, A, positioned in the center of a disk, B, graduated in degrees on the periphery. The disk can be rotated about its axis and the degrees of rotation read from a vernier scale, C. The hairline image was projected along with the images of the slide surface and the drop through a microscope equipped with a Wetzler 5X adapter, D, instead of an eyepiece. The objective of the microscope was a 32-mm. objective, E, with an adjustable diaphragm which was closed almost completely to obtain the depth of field necessary to superimpose in focus the hairline and the drop profile. The contact angle was measured by positioning the drop so that it was tangent to the hairline at the intersection between the drop and the slide surface, F. The contact angle was then determined from the number of degrees of rotation of the disk. The drop was also photographed by attaching a Leica camera, G, as shown in Fig. 8. The negative was enlarged and the contact angle measured with a protractor. Both the direct reading and photographic techniques gave comparable results for the contact angle between water and paraffin (see Table X). Thus, the direct-reading procedure was used throughout the study because it was more rapid.

The volume of the wetting liquid used to determine the contact angle was 10 λ. The manner in which the wetting liquid was placed on the surface affected the contact angle. The latter varied depending upon whether the drop was released while the periphery was advancing or receding over the monolayer surface. The advancing angle was slightly larger than the receding angle as would be expected in light of the previous discussion concerning the factors which influence the contact angle. The advancing angle proved to be the more reproducible, and, thus, the drops were

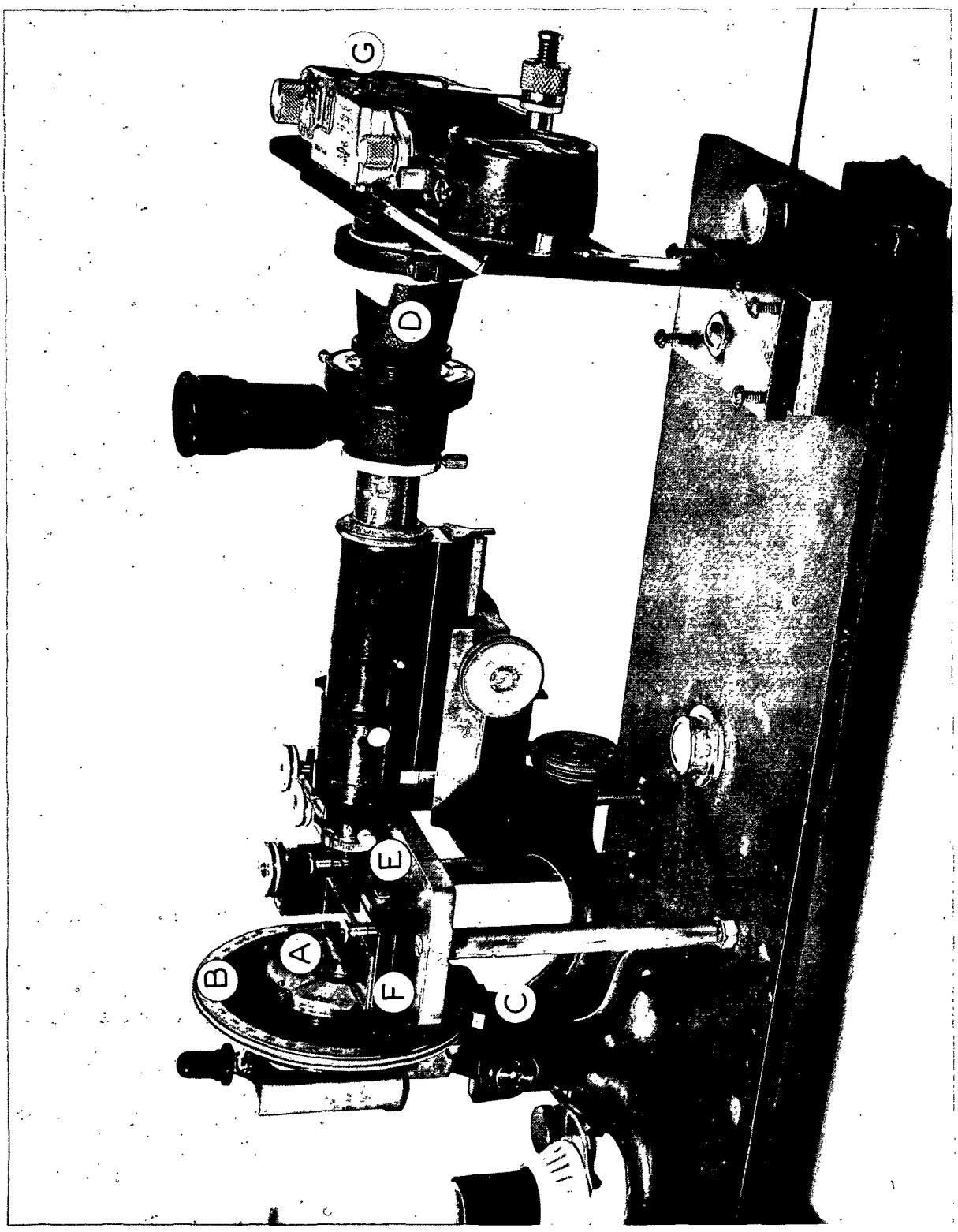

Figure 8. Apparatus for Measuring Contact Angles

TABLE X

CONTACT ANGLE BETWEEN WATER AND PARAFFIN

Direct Method		Photographic Method	
Drop No.	Contact Angle,°	Drop No.	Contact Angle,°
1	103.0	1	101.0
2	102.3	2	102.0
3	102.8	3	102.5
4	102.8	4	102.0
5	103.2	5	103.5
6	101.6	6	102.5
7	102.5	7	102.5
8	102.2	8	100.5
9	102.3	9	102.5
10	101.3	10	102.5
Mean	102.4	Mean	102.2
Variance	0.356	Variance	0.724

released while the periphery was advancing over the surface. The contact angle was measured approximately 30 seconds after the drop was released. Although the time lapse was somewhat arbitrary, it appeared long enough to allow redistribution of the unoxidized linoleic acid, but not so long that extraneous effects were introduced by evaporation of the liquid or by chemical modification of the material in the monolayer. The choice of a time lapse of 30 seconds also seems justified in view of Yiannos's (48) work. Yiannos found that multilayers of lauric acid, which would have a molecular mobility approaching that of linoleic acid, reached an equilibrium contact angle within 10 seconds. Therefore, the contact angle, measured in this work can best be described as an advancing initial equilibrium

contact angle. The standard error of the contact angle in the range from 10 to 105 degrees was about $\pm$ 1°. Contact angles below 10 degrees were too small to measure.

DISCUSSION OF RESULTS

PRESSURE-AREA ISOTHERM OF LINOLEIC ACID

The pressure-area isotherm of linoleic acid was measured in order to ascertain at what film pressure to transfer the monolayer to the solid surface so as to obtain the most compact monolayer. For a review of the theory underlying the pressure-area isotherms of monolayers of insoluble fatty acids see Appendix I.

The concentration of the linoleic acid in the spreading solution was varied from 0.874×10^{-2} M to 0.874×10^{-3} M to determine whether the solvent was irreversibly held in the monolayer. La Mer and Robbins (101, 102) found that ethyl ether, petroleum ether, hexane, and benzene were all irreversibly retained in a stearic acid monolayer after spreading. The retention of the solvent resulted in an increase in the area per molecule of about 8 to 10%, at 1 dyne per cm. pressure, and the expansion was greater the more dilute the solution. However, an expansion of the linoleic acid monolayer was not evident even for a tenfold change in the concentration as shown in Fig. 9. The data from both solutions agreed within the experimental error. Thus, either the hexane was not irreversibly retained in the linoleic acid monolayer or, if retained, it did not cause a significant expansion.

Because the pressure-area data for linoleic acid were unavailable in the literature, the pressure-area isotherm of oleic acid was measured in order to check the experimental techniques. The isotherm agreed well with that obtained by Marsden and Rideal (103) on 0.001N HCl at 21°C. as shown in Fig. 10. The isotherm was more expanded than that measured by Marsden and Rideal but this may have been because they measured the isotherm at a slightly lower temperature and their substrate was at a pH of 3.

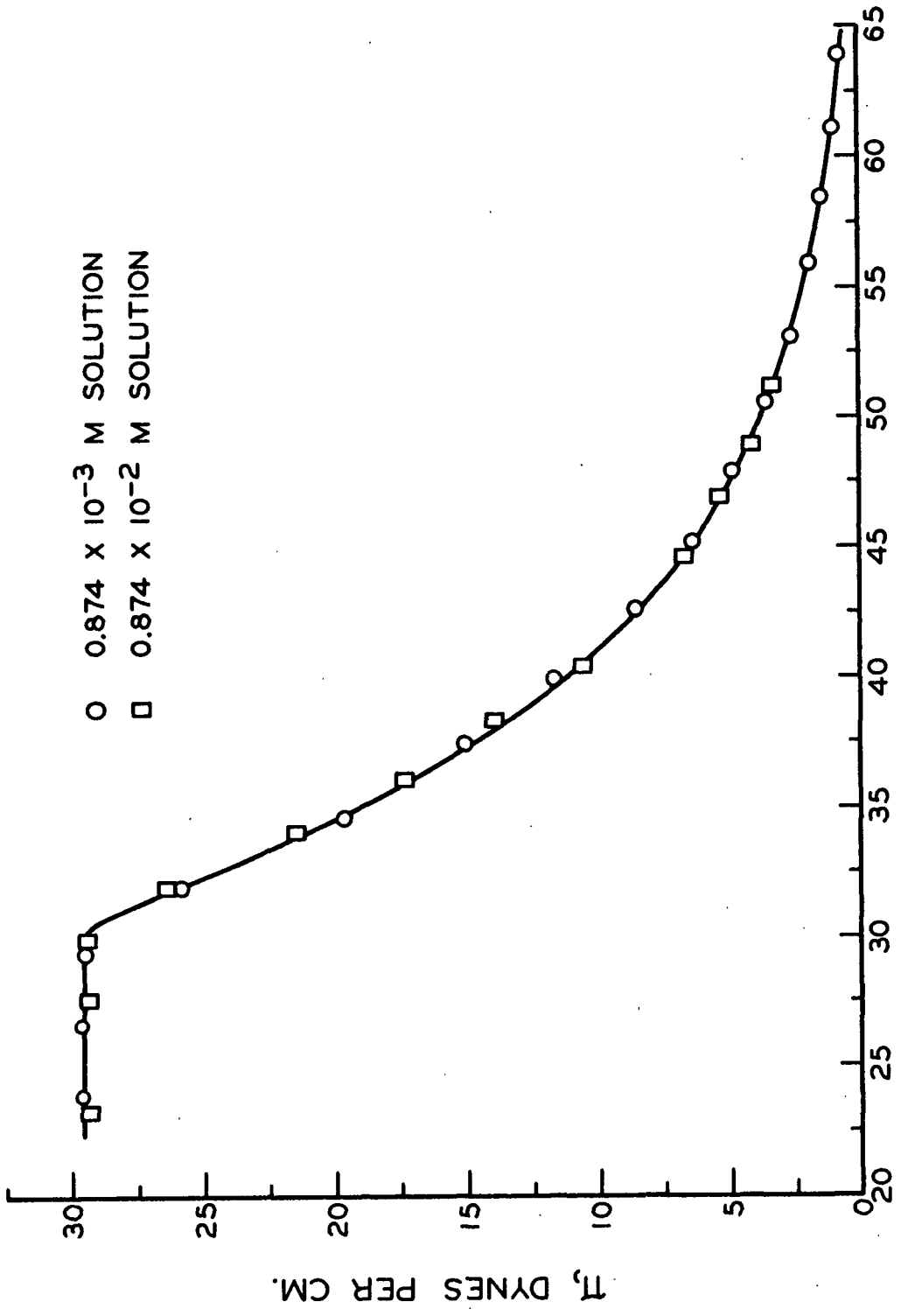

Figure 9. Pressure-Area Isotherm of Linoleic Acid at 22 ± 0.5°C. on 0.01N HCl

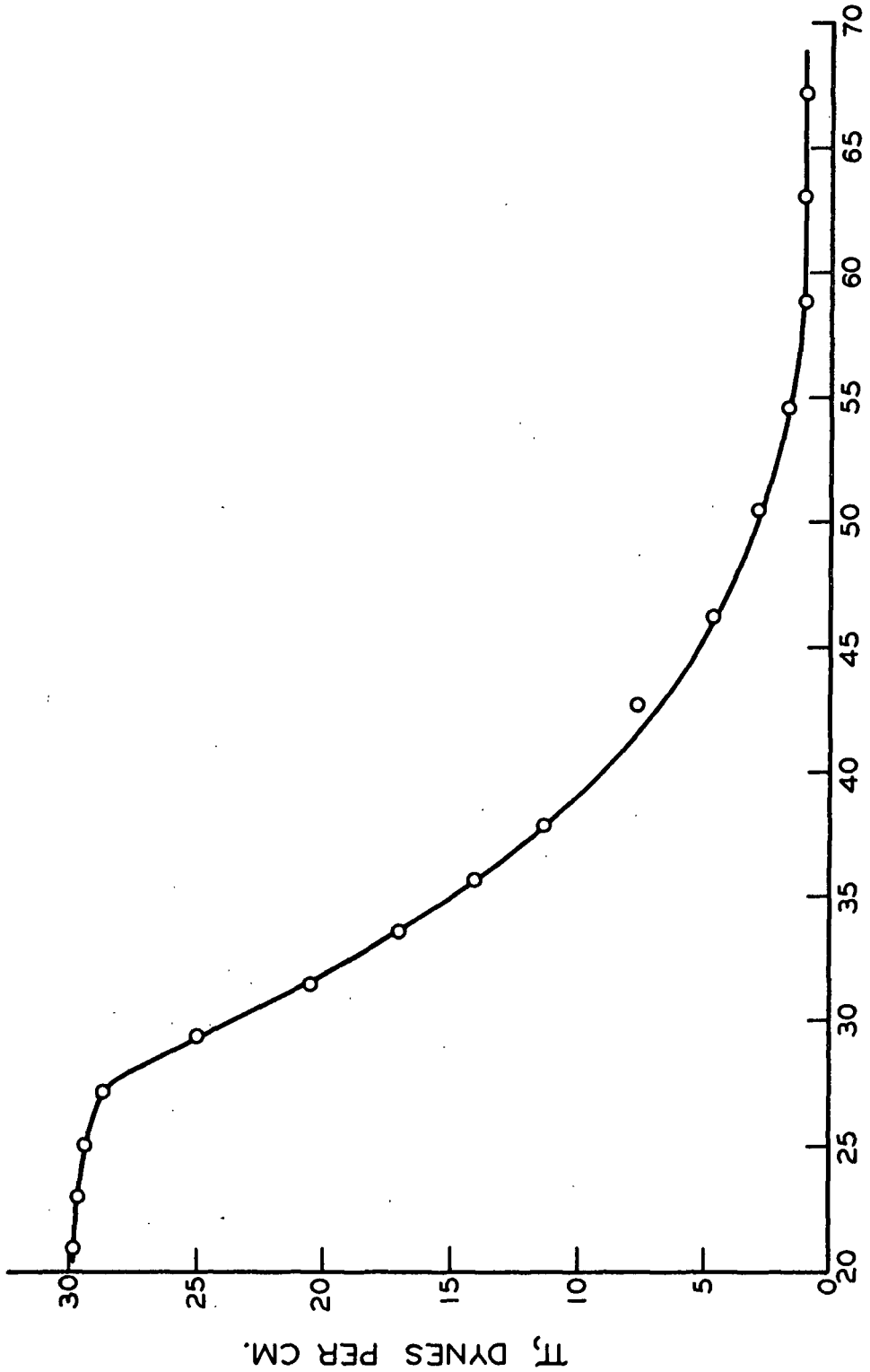

Figure 10. Pressure-Area Isotherm of Linoleic Acid at 22 ± 0.5°C. on Distilled Water

The linoleic acid isotherms were definitely of the expanded type (104, 105). The expanded films are considered to be analogous to but much more compressible than liquids in the three-dimensional state. If the film is below the critical point, upon compression from the gaseous state it will pass through a two-phase region in which the expanded film is in equilibrium with the gas phase. In this region the pressure remains constant as the film is compressed. This is a first-order change which is accompanied by an evolution of heat. Once in the liquid expanded state, the isotherm exhibits nearly a hyperbolic relationship. As compression is continued it may exhibit a second-order change (a discontinuity in pressure without one in area) and change to a solid film by passing through an intermediate state. However, if the molecular attraction is insufficient, this second-order transition is not observed and the film collapses to form islands of the three-dimensional liquid in equilibrium with the two-dimensional liquid state. When the monolayer is above its critical temperature, the first-order change is also unobserved and the film passes smoothly from the gaseous state to the liquid expanded state. The isotherm for the linoleic acid on the distilled water substrate, pH 6.5, showed definitely a first-order change at about 59 $A.^2$ per molecule, and a collapse point at about 26 $A.^2$ per molecule (see Fig. 11). The first-order change for the isotherm on the 0.01N hydrochloric acid solution was not well defined because the pressure was too low. However, the collapse point was well defined at 30.5 $A.^2$ per molecule as shown in Fig. 9. The isotherm on the distilled water was more condensed than the one on the dilute hydrochloric acid, except at the higher molecular areas. Presumably, this was due to trace amounts of cations which are able to complex with the carboxyl groups causing contraction of the film.

Langmuir (106) developed a theoretical relationship for the pressure-area isotherms of expanded films. The upper surface was assumed to have the same tension as a hydrocarbon oil against air, and the lower surface was assumed to be

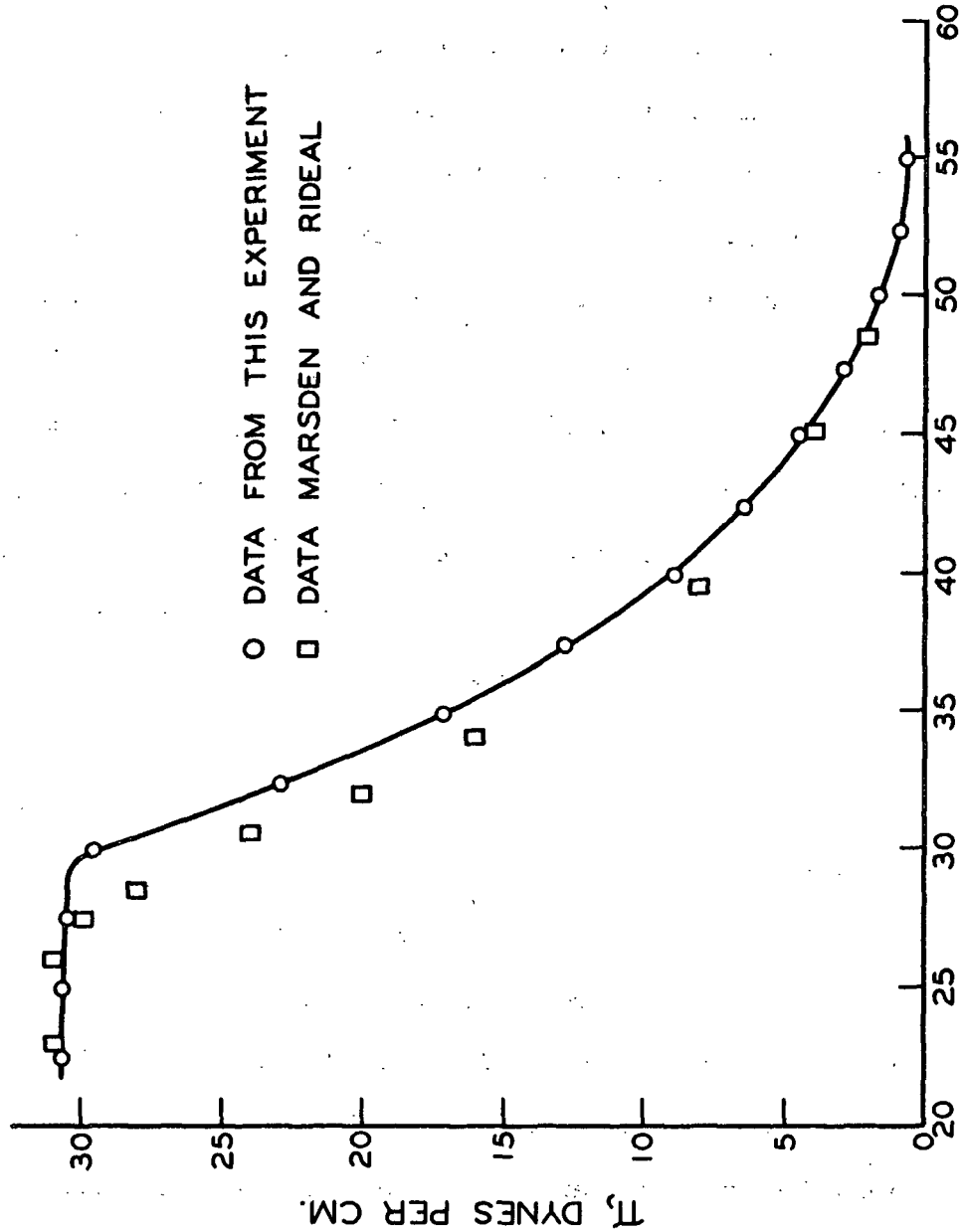

Figure 11. Pressure-Area Isotherm for Oleic Acid at 22 ± 0.5°C. on 0.01N HCl

a gaseous film of the water-soluble carboxyl groups. The hydrocarbon portion of the film was considered to be in chaotic motion. The spreading force of the duplex film was then considered to be the sum of the spreading pressures of the hydrocarbon chains and of the gaseous film of the water-soluble carboxyl groups. The spreading pressure of the hydrocarbon chains was represented as follows:

$$\pi_o = \gamma_{water} - \gamma_{water\text{-}oil} - \gamma_{oil} \tag{29}$$

For the carboxyl groups the pressure was represented by the following equation:

$$\pi_g(\sigma\text{-}b) = kT \tag{30}$$

where $\underline{k}$ is the Boltzman Constant, σ is the area per molecule and $\underline{b}$ is a constant related to the area actually covered by the carboxyl group. The total spreading force, was considered as the sum of the above two expressions, which results in the following equation:

$$(\pi - \pi_o)(\sigma\text{-}b) = kT \tag{31}$$

However, the constants, π_o and $\underline{b}$, are actually empirical, and do not have a large amount of theoretical significance.

The isotherm of the linoleic acid monolayer on the 0.01$\underline{N}$ hydrochloric acid solution was fitted to Equation (31), to the two-dimensional ideal gas law and also to the gas law in the form of a virial equation to account for deviations from ideality. The ideal gas law fails to describe the data as might be expected, as shown in Fig. 12. Attractive forces between the molecules cause the pressure to be lower than expected at the higher areas per molecule and the repulsive forces cause the pressure to be higher than expected at the lower molecular areas.

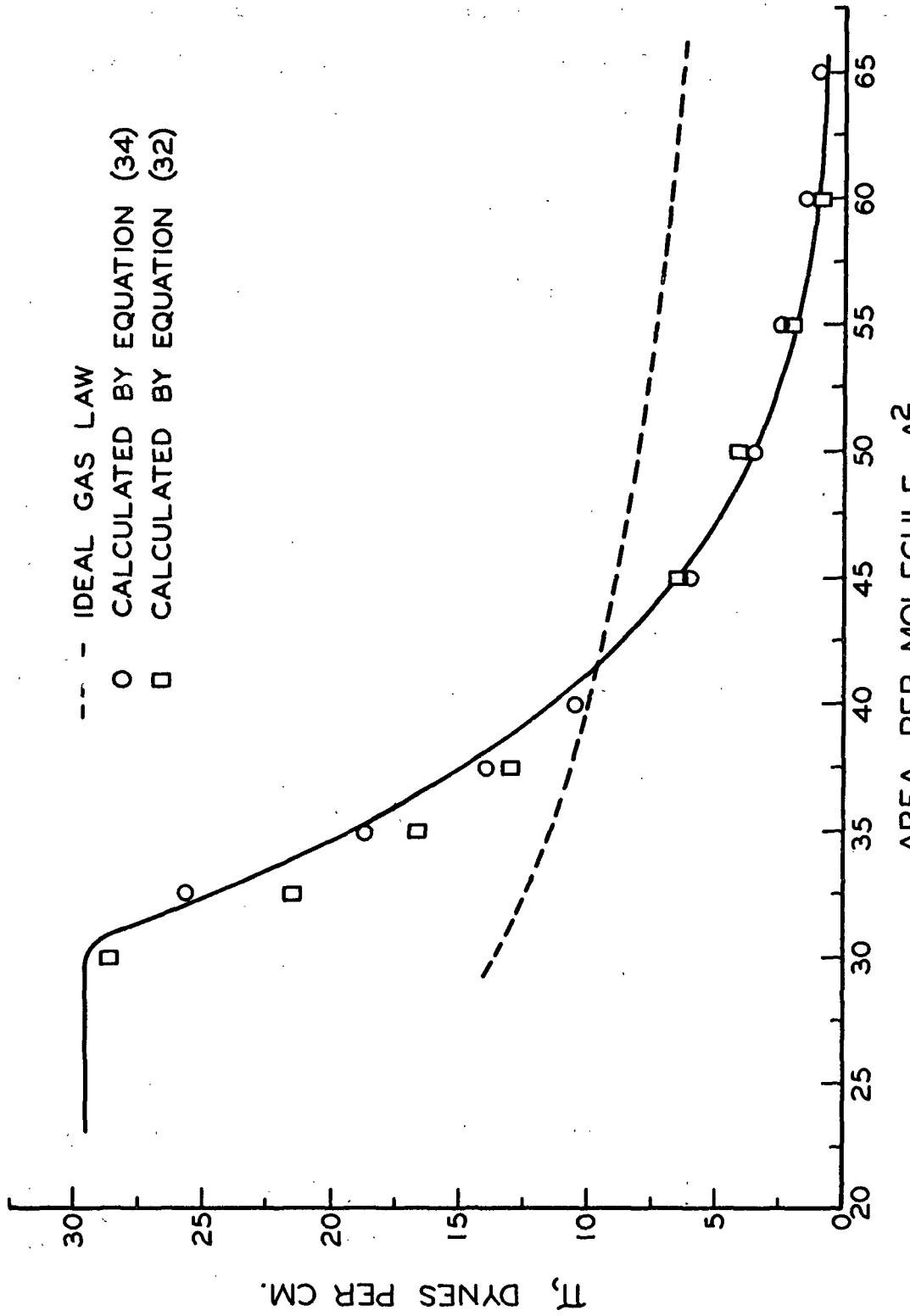

Figure 12. Pressure-Area Isotherm of Linoleic Acid at 22 ± 0.5°C. on 0.01N HCl

Equation (31) can be made to fit the data in either the high or low pressure region but not both at once. The lack of agreement over the entire isotherm resulted because the constants, π_o and $\underline{b}$, were a function of the area per molecule. Values of π_o and $\underline{b}$ were so chosen that the calculated points fit the isotherm in the low pressure region, and the final equation was as follows:

$$(\pi+9.3)\ (\sigma-19.3) = kT \qquad (32)$$

However, the data were described quite well over the whole isotherm by using the two-dimensional gas law in the form of a virial equation. The equation was as follows:

$$\pi\sigma/kT = 1 + k_1/\sigma + k_2/\sigma^2 \qquad (33)$$

$$\pi\sigma/kT = 1 - 141.5/\sigma + 5698/\sigma^2 \qquad (34)$$

The second term accounts for the attractive forces between the molecules, and the third for the repulsive forces when the area per molecule was quite low. When Equation (33) was fitted to the oleic acid isotherm, $\underline{k}_1$ increased about 6.9% and $\underline{k}_2$ 0.6% over the values for the linoleic acid isotherm, indicating that the differences in the two isotherms were caused mainly by changes in the attractive forces.

In summary, the pressure-area isotherms of linoleic acid on dilute hydrochloric acid and on distilled water were of the expanded type. The isotherm was slightly more expanded on the dilute hydrochloric acid substrate than on distilled water. Equation (31) developed by Langmuir and the two-dimensional gas law written in the form of a virial equation described the data fairly well.

TRANSFER OF MONOLAYERS TO THE SOLID SURFACES

Compounds which form solid monolayers on the aqueous substrates apparently retain the same area per molecule when transferred to a solid surface. Langmuir, et al., (107) found that the ratio of the area per molecule on the solid to that on the water surface varied between 0.98 and 1.00 for a number of compounds such as cholesterol, cholestanol, and barium stearate. Gaines (108) found that the count of 1-C^{14} labeled stearic acid when on the aqueous substrate agreed with the count of the monolayer after it had been transferred to a mica plate and that both counts were in agreement with the area per molecule calculated from the pressure-area isotherm. The agreement held quite well over the entire isotherm. Apparently, for monolayers which are solid on the aqueous substrate, the cohesive forces between the molecules are sufficiently great to allow the monolayer to bridge over irregularities of the solid surface during transfer. Since linoleic acid forms an expanded film, the following experiments were conducted to determine whether the area per molecule was retained upon transfer as in the case of the solid films.

DEPOSITION ONTO A GLASS SURFACE

The linoleic acid monolayers were deposited at various film pressures from about 28.2 dynes per cm. to 3.71 dynes per cm. The radioactive count of the monolayer on the glass surface was then plotted against the reciprocal of the area per molecule before transfer, as determined from the pressure-area isotherm.* If the area per molecule before and after transfer was unaltered, a linear relationship would be obtained up to the point of collapse of the monolayer. At this point there would be a large increase in the radioactive count with little change in area. However, although the relationship was linear, the area per molecule where

*All the monolayers were transferred to the solid surfaces from the dilute hydrochloric acid substrate so that the carboxyl group would not be ionized.

the large increase in the radioactive count occurred was greater than the area per molecule at the collapse point of the monolayer (see Fig. 13). The area per molecule, where the large increase in the radioactive count was noted, was between 31.9 $A.^2$ ($1/A.^2$ = .0313) and 31.3 $A.^2$ ($1/A.^2$ = .0320) while collapse occurs at 30.2 $A.^2$ ($1/A.^2$ = .0331). The data indicate that either (1) the area per molecule on the glass and aqueous surfaces were the same but collapse to a three-dimensional structure occurred sooner on the glass, or (2) that the area per molecule on the glass was proportional to, but less than the corresponding area per molecule on the aqueous substrate and the area per molecule at which collapse commences was the same for both surfaces.

To resolve the foregoing question, monolayers of 1-C^{14} stearic acid of a known specific activity were deposited and the radioactive count compared with that of the linoleic acid monolayers. The area per molecule on an aqueous substrate of a compact stearic acid film has been established as 20.5 $A.^2$ per molecule (104) and the area per molecule is retained upon transfer to a nonreactive solid surface as discussed previously. Therefore, it was possible independently to calculate the area per molecule of the linoleic acid on the glass surface knowing the specific activities of the stearic and linoleic acids (see Appendix VI). The area of the linoleic acid on the glass was calculated for the point at which the curve breaks and exhibits the large increase in the radioactive count. The area was 30.5 $A.^2$ per molecule which was the same as the area per molecule at the collapse point of the monolayer. Probably such close agreement was fortuitous. However, it does appear that the area per molecule on the glass surface was proportional to, but not equal to, the corresponding area per molecule on the aqueous surface; the monolayer being somewhat more condensed on the glass surface. Also, the area per molecule where formation of a three-dimensional structure begins was evidently the same for both the glass and aqueous surface. Thus, in order to obtain the most

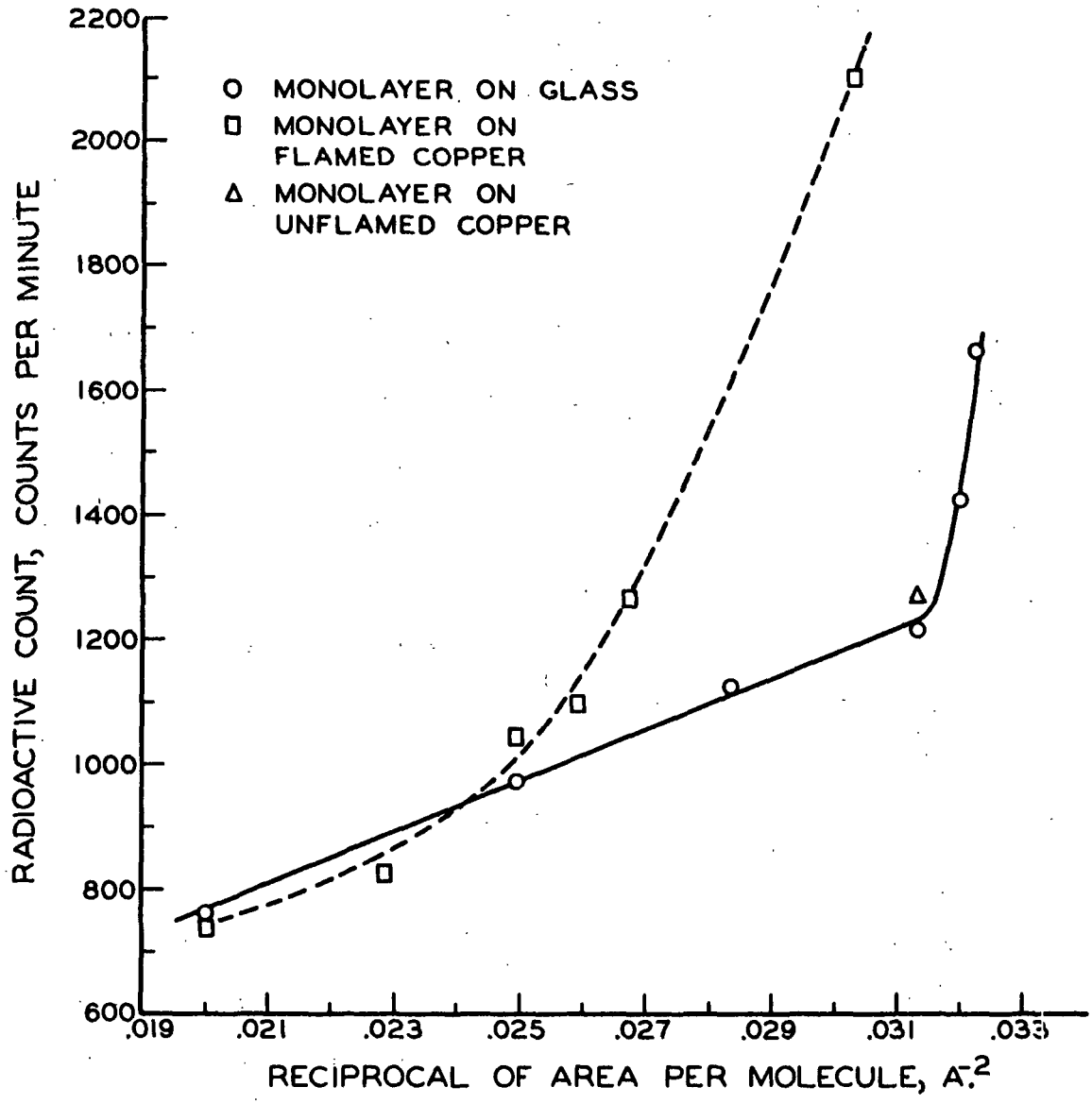

Figure 13. Reciprocal of Area Per Molecule on Aqueous Substrate Versus Count of Monolayer on Solid Surface

compact monolayer possible without multilayer formation, every deposition onto a glass surface was carried out at 26.0 dynes per cm. which corresponded to an area of 32.0 A.^{2} on the aqueous surface and 30.5 A.^{2} on the glass surface.

DEPOSITION ONTO A COPPER SURFACE

The relationship between the area per molecule on the copper surface and that on the aqueous substrate depended upon the method of cleaning the copper surface. When the copper plates were removed from the hot benzene and the remaining benzene allowed to evaporate, the radioactive count of a linoleic acid monolayer deposited at 26 dynes per cm. was comparable to that on glass after correcting for the increased backscattering of the copper[1] (see Fig. 13). However, when the copper was flamed to remove the last traces of the benzene,[2] the count was much greater and the area per molecule on the copper was no longer proportional to the area on the aqueous substrate. Multilayer deposition now commenced at low film pressures. When the copper surfaces were not flamed, the residual benzene evidently prevented the carboxyl group from reacting with the copper. Therefore, the relationship between the area per molecule of the linoleic acid on the copper and aqueous surface was the same as for the glass. However, when the carboxyl group could react chemically with the surface, the driving force for multilayer formation was greater, and multilayers were formed at low film pressures.[3]

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[1] The backscattering coefficient was calculated by depositing a monolayer of stearic acid on both copper and glass and determining the ratio of the counts assuming that the backscattering of the glass was equal to one. The backscattering coefficient was found to be 1.16 which compares favorably with the value of 1.18 determined by Yiannos (48).

[2] Water did not wet the copper surface after the residual benzene evaporated indicating that at least a benzene monolayer was present.

[3] Gottlieb (109) found that adsorbed organic solvents stabilized clean metal surfaces against the further adsorption of organic molecules from the atmosphere, as indicated by the contact potential. Thus, it is reasonable to expect that the residual benzene prevented the formation of multilayers and that flaming did not activate the surface other than to make it very clean.

However, the area per molecule of the stearic acid, which forms a solid monolayer on the aqueous substrate, was the same on both the flamed and unflamed copper surfaces and evidently was also equal to the area per molecule on the aqueous surface. Thus, even though the carboxyl group of the stearic acid could react with the flamed copper, the solid state of the monolayer apparently prevented the formation of multilayers. Therefore, it appears that multilayer formation was due both to the reaction of the carboxyl group with the copper surface and to the motion of the hydrocarbon chains of the linoleic acid which probably permitted interpenetration of the molecules.

All of the linoleic acid monolayers, which were analyzed with regard to the contact angle with water, were deposited onto flamed copper so that the residual benzene would not interfere with the magnitude of the angle. As shown in Fig. 13, the concentration on the copper surface was a large function of the film pressure when the coverage approximated a monolayer. Thus, small changes in the condition of the surface or small errors in the film pressure could cause relatively large differences in the concentration of the linoleic acid on the surface. As a result, the reproducibility of deposition was not nearly as good as when the monolayers were deposited onto glass (see Table VII). In order to be sure that multilayers were not formed, the concentration was purposely kept somewhat below a compact monolayer. The deposition pressure was 13.0 dynes per cm., which gave an average area per molecule on the copper of 33.7 $A.^2$

AUTOXIDATION OF THE MONOLAYER ON A NONREACTIVE SURFACE

AUTOXIDATION IN THE ABSENCE OF WATER VAPOR

The monolayers were aged on a nonreactive glass surface so that changes in the monolayer structure which occurred during autoxidation would have the maximum

effect on the contact angle and not be masked by a large attraction between the carboxyl group and the substrate. Aging was carried out in the absence of water vapor, to eliminate the possibility that water molecules trapped in the monolayer might alter the specific free surface energies of the system.

Rate of Autoxidation

Data on the rate of autoxidation in the absence of water vapor were not sufficiently precise to permit analysis. The time required to reach a given level of autoxidation varied from monolayer to monolayer and especially between monolayers which were not formed on the same day. Small changes in the concentration of the molecules on the surface did not appear to alter the rate of oxidation. Evidently, small amounts of impurities with antioxidant properties or differences in the concentration of free radicals were responsible for the variable rate of autoxidation. Another factor which made the interpretation of the rate data difficult was the high initial autoxidation. About 20% of the monolayer was autoxidized immediately after deposition of the monolayer.* The time required to deposit the monolayer was about four minutes and the time required to analyze the amount of oxidation was about 20 minutes. Thus, within 25 minutes about 20% of the monolayer was autoxidized. Approximately 40 hours were required to cause a further oxidation of 20%. Part of the initial oxidation may have been due to the retention in the monolayer of oxidized linoleic acid which was formed by autoxidation of the hexane solution. The linoleic acid in the hexane solution was autoxidized even though the solutions were stored in the dark, under nitrogen and in the refrigerator. However, the amount of oxidation which occurred in solution did not affect the initial amount of autoxidation of the monolayer as shown by the data in Table XI.

*It is unlikely that the high initial amount of oxidation is the result of errors in the analyses. Both the hexane insolubility method and the chromatographic method agreed well at zero time of aging and it is not likely that 20% of the acid was oxidized during the time required for chromatographic separation (98).

TABLE XI

THE INITIAL AMOUNT OF AUTOXIDATION OF THE MONOLAYER AS AFFECTED BY OXIDATION OF THE SPREADING SOLUTION

Monolayer No.	Oxidation of Spreading Solution, %	Initial Amount of Autoxidation of the Monolayer, %
48-1	3.6	21.3
45-1	8.8	19.3
42-1	16.2	17.3

Evidently, the oxidized linoleic acid escaped into the 0.01N HCl substrate when the monolayer was first spread and in the expanded state. Thus, the initial 20% of autoxidation evidently occurred during the 25 minutes required for depositing and analyzing the monolayer. This high initial rate of autoxidation may have been due to trace amounts of an oxidant in the water, possibly potassium permanganate, or possibly to exposure to light during the deposition, which was excluded when the monolayers were aged further on the glass surface.

However, even though the data were erratic, the rate of autoxidation appeared to be less rapid in nitrogen than in air. After 154 hours of oxidation in nitrogen only about 30% of a monolayer had been autoxidized whereas from 40 to 65% of a monolayer was autoxidized in an equivalent time period in air. The decrease in the rate of autoxidation in nitrogen is in agreement with the findings on bulk systems (73).

Contact Angle Between Water and the Autoxidized Monolayer

The material formed during the autoxidation of the monolayers in dry air increases the contact angle with water from zero at about 15% oxidation to about 56° at 65% oxidation. The contact angle with the unoxidized acid was apparently zero. The relationship between the cosine of the angle and the amount of autoxidation of

the monolayer is shown in Fig. 14. The contact angle with only the oxidized material was also determined. The unoxidized acid was removed with hexane and the area of the glass surface formerly occupied by it was exposed to the water. The relationship between the cosine of the angle and the amount of oxidized linoleic acid on the surface is essentially the same as the relationship between the cosine of the angle and the amount of autoxidation of the monolayer as shown in Fig. 14 and 15.[1] Because these two relationships are essentially the same, the wettability of the unoxidized portion of the monolayer was evidently the same as the wettability of the exposed high energy glass surface. Therefore, the unoxidized linoleic acid was ineffective in lowering the specific free surface energy of the glass (with regard to water) irrespective of its concentration in the monolayer.

As indicated previously, the water was not expected to form a finite contact angle with the completely unoxidized monolayer because it undoubtedly was in the liquid state and the attraction of the carboxyl group and the water for the glass was of the same order of magnitude.[2] Evidently, these monolayer properties tend to promote: (1) diffusion of the water into the monolayer; (2) overturning of the molecules so that the carboxyl group is at the water monolayer interface; and (3) spreading of the linoleic acid on the water surface, all of which decrease the contact angle. However, because the unoxidized acid was not effective in increasing

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[1] The cosines of the contact angles against just the oxidized linoleic acid are actually slightly lower than the cosines of the angles with the complete monolayer at all levels of oxidation. However, if the cosine of the angle between just the water and the exposed glass surface was assumed to be about 0.946 instead of one, the decrease in the cosine of the over-all angle could be accounted for. Apparently, either the water does not contact the glass surface completely in the exposed areas and therefore forms a water-air interface, or some hexane is retained in these areas which lowers the free energy of the glass surface.

[2] As an example, a monolayer of oleic acid which is above its melting point at room temperature does not form a finite contact angle with water when spread upon glass.

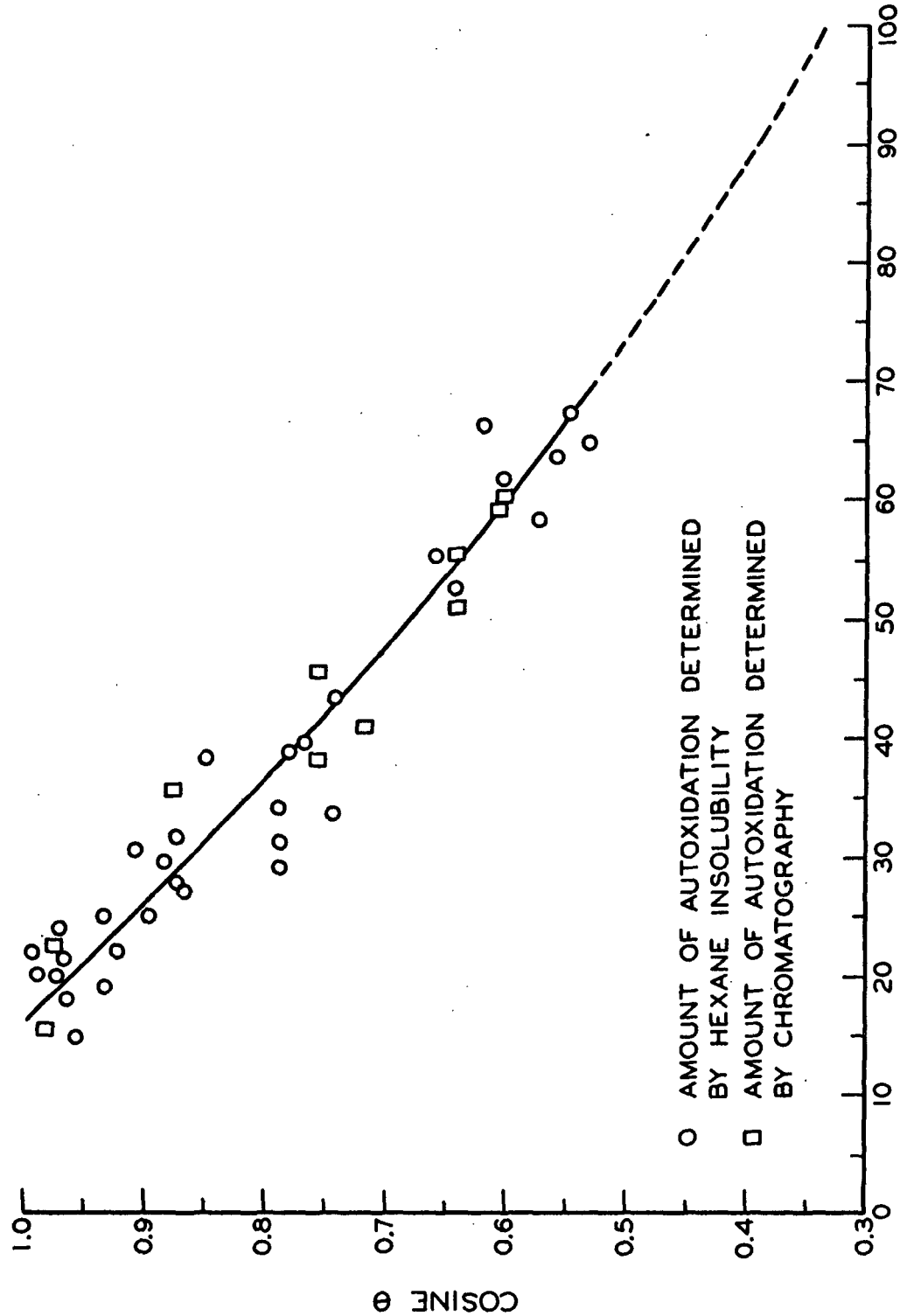

Figure 14. Cosine of the Contact Angle with Water as a Function of the Amount of the Monolayer Autoxidized

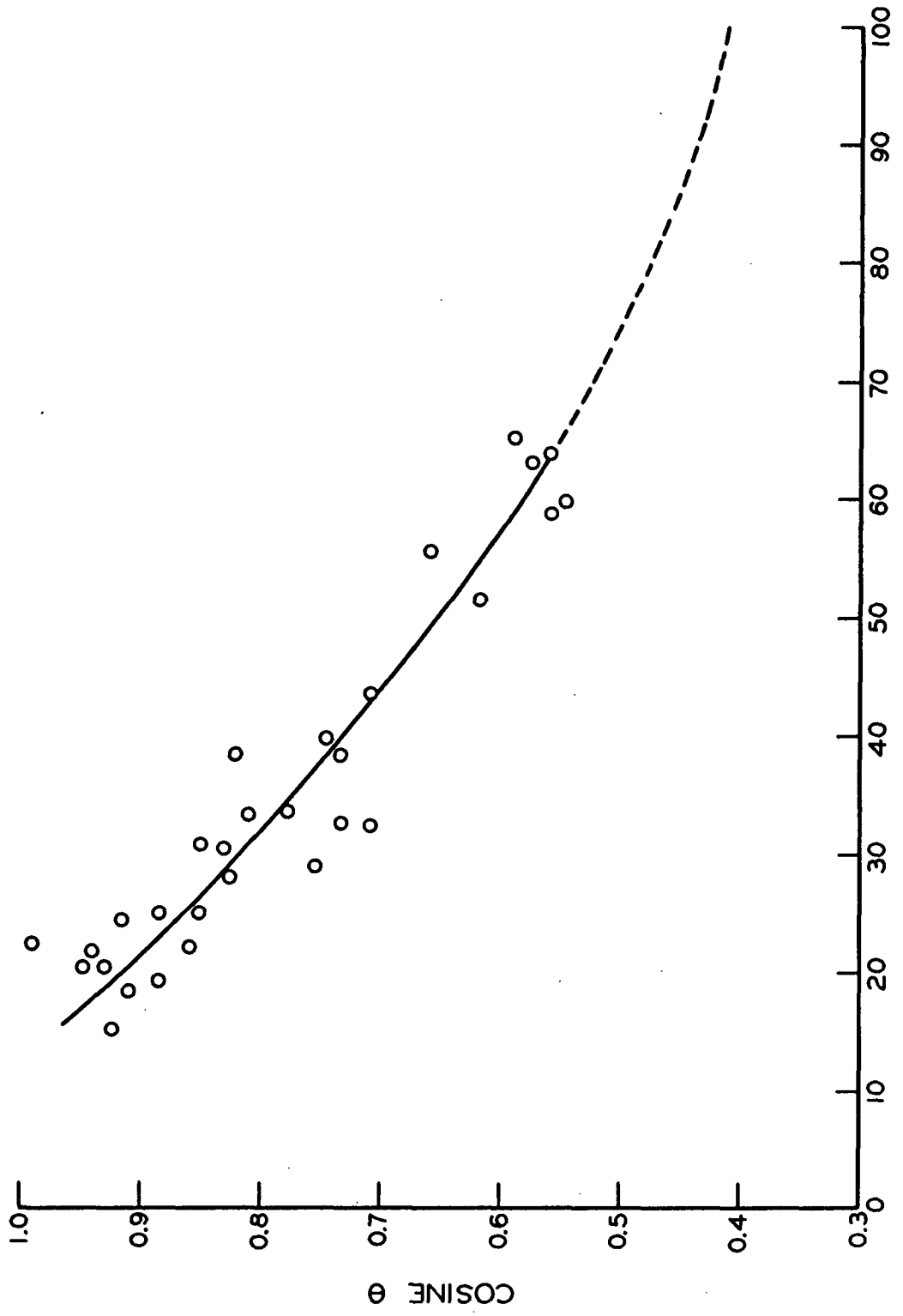

Figure 15. Cosine of the Contact Angle Between Water and the Products of Oxidation as a Function of Surface Coverage

the contact angle irrespective of its concentration in the monolayer, it was possible to make certain deductions as to which of the above phenomena were most important in this system.

The contact angle between a completely unoxidized monolayer and water is related to the specific free surface energies of the system as indicated by the Young-Dupre Equation

$$\text{cosine } \theta = (\gamma_S - \gamma_{SL})/\gamma_{LV}. \qquad (4)$$

However, when the monolayer is disturbed by the wetting liquid the free energy terms are poorly defined. Specifically, γ_{SL} is readily decreased. However, even if the interfacial tension was zero, a finite contact angle would still be formed as long as γ_{LV} was greater than γ_S. Therefore, a decrease in only γ_{SL} cannot account for the contact angle being zero against the unoxidized monolayer. However, if the linoleic acid under the drop was to spread on the surface of the drop and form a close-packed monolayer, γ_{LV} could be decreased to about 43 dynes per cm. The surface tension of the water might then be nearly equal to the specific free energy of the monolayer-air interface and thus permit spreading of the water over the monolayer surface. Changes in γ_{LV} might account for the contact angle being zero against the completely unoxidized monolayer. However, changes in γ_{LV} evidently cannot account for the unoxidized acid being ineffective in increasing the contact angle once the monolayer becomes appreciably oxidized.

As autoxidation proceeds and the monolayer becomes heterogeneous, changes in γ_{LV} apparently become less important as will now be discussed. The contact angle against the heterogeneous monolayer may be considered as the sum of the individual specific free surface energies of the various groups of molecules making up the monolayer. The following relationship can then be written for the heterogeneous

monolayer by manipulating Equation (8) assuming that the projected area per molecule in the monolayer surface is the same for both the oxidized and unoxidized fractions.

Then

$$\text{cosine } \theta = (x)(\gamma_{S1}-\gamma_{SL1})/\gamma_{LV} + (1-x)(\gamma_{S2}-\gamma_{SL2})/\gamma_{LV} \quad (35)$$

$$\text{cosine } \theta = (x) \text{ cosine } \theta_1 + (1-x) \text{ cosine } \theta_2 \quad (36)$$

where γ_{S1} and γ_{SL1} are the specific free energies of the oxidized fraction, γ_{S2} and γ_{SL2} are the specific free energies of the unoxidized fraction; and x is the fraction oxidized. It follows from these definitions that θ_1 and θ_2 are the contact angles against the oxidized and unoxidized fractions, respectively. γ_{LV} appears in both terms on the right-hand side of Equation (35). Therefore, large changes in γ_{LV} could not have occurred because the oxidized material would then be relatively ineffective in increasing the contact angle. Also, as oxidation progresses the fraction of the monolayer under the drop, which has to spread on the drop surface in order to lower γ_{LV}, increases markedly. This occurs, because the ratio of the area of the drop surface to the area under the drop increases as the contact angle increases. Thus, to decrease the surface tension just 5 dynes per cm., order of magnitude calculations indicate that the monolayer would have to be depleted by 69% at 20% oxidation and by 80% at 50% oxidation (see Appendix VI). Thus, a large decrease in γ_{LV} caused by spreading of the monolayer material on the drop surface does not seem to be the most important factor influencing the contact angle. Autoradiographic data support this conclusion. Drops of water were placed on monolayers which were autoxidized various amounts and then removed with a thin capillary. Any material which had spread on the drop surface was undoubtedly removed with the water. The amount of the monolayer which was removed with the drop was determined by analysis of changes in the optical density of the film plate. The data, presented in Table XII, show that the amount of material

which could have spread on the water surface was not sufficient to cause a large decrease in γ_{LV}.

TABLE XII

ANALYSIS OF THE EXTENT OF REMOVAL OF THE MONOLAYER BY A RECEDING DROP OF WATER

Monolayer No.	Contact Angle, degrees	Oxidation, %[a]	Removed, %
96-1	20	21.5	76.8
96-3	38	37.5	36.5
93-6	48	51.0	33.9
93-3	58	69.0	33.9

[a]The per cent oxidation was obtained from the contact angle data in conjunction with the relationship shown in Fig. 14.

Apparently, the inability of the unoxidized linoleic acid to prevent the wetting of the glass surface by water can be explained better by a much higher specific free surface energy for the unoxidized portion of the monolayer than would be expected from the structure of the molecule. The monolayer free surface energy could be increased if the carboxyl groups of the unoxidized acid were oriented away from the glass surface and located at the monolayer-air interface. However, free energy considerations make such a condition highly improbable. A more plausible explanation is that because of the high degree of motion of the molecules and because the attraction of the water and carboxyl group for the glass surface were nearly the same, a stable boundary between the hydrocarbon chains of the unoxidized acid and the water was not formed. Apparently, the water diffused more rapidly through the unoxidized portion of the monolayer (and/or along the interface between the unoxidized part of the monolayer and the glass) than the periphery of the drop advanced over the monolayer surface. The effective

specific free surface energy of this portion of the monolayer at the drop boundary would then be that for the monolayer filled with water. Therefore, it could be as high as the surface tension of the water and a finite contact angle with the unoxidized portion of the monolayer would not be formed. However, if the oxidation reduced the motion of the molecules to the point where they were in the solid state, the coherent structure would tend to force the water to break a large number of intermolecular bonds at one time in order to diffuse through the oxidized monolayer or spread at the monolayer-glass interface. Therefore, the greater activation energy required for diffusion would favor the formation of a stable boundary between the outermost surface of the oxidized material and the drop, and the magnitude of the contact angle with this material would be controlled by the nature of the groups in its outermost surface. In brief, it appears that diffusion of the water into the unoxidized portion of the monolayer and its resultant effect on γ_S was the most important factor in decreasing the over-all contact angle.

From the foregoing discussion it is evident that the degree of autoxidation of the monolayer, and the ability of the oxidized material to form a solidlike coherent structure with a low free energy outermost surface was most important in increasing the contact angle. The effect of increasing the concentration of the oxidized material is apparent from Equation (36). If there were no interaction effects and the products of autoxidation were homogeneous, the contact angle would increase linearly with increasing concentration. The relationship between cosine θ and the amount of oxidation was actually somewhat curved (see Fig. 14). However, it did not deviate from a linear relationship as markedly as did the data of Bartell and Ruch (36) for water against depleted monolayers of n-octadecylamine.

The curvature cannot be attributed solely to a breakdown of Equation (36). All of the oxidation products may not be equally effective in increasing the

contact angle. The oxidation products produced in the early stages of oxidation were probably not as highly oxidized as in the later stages. That is, the number of oxygen molecules per molecule of oxidized acid in the initial stages was lower than in the later stages of oxidation. Presumably, the initial oxidation products were continually being oxidized to secondary products which probably were better able to form a stable interface with the water. Thus, the decrease in the contact angle to zero at 15% oxidation may have been due partly to the inability of the initial oxidation products to form a coherent, solidlike structure. Undoubtedly, the heterogeneity of the oxidation products contributed to the scatter in the data.

The maximum contact angle would be obtained if the oxygen groups, introduced during oxidation, were not present in the outermost surface of the monolayer. Extrapolation of the curve in Fig. 14 to 100% oxidation indicates that the contact angle against the completely oxidized monolayer would be about 71°. This angle is of the order of magnitude of that for water against nylon (110), which has numerous hydrophilic groups in the surface. In contrast, the contact angle with polyethylene, whose surface is composed of methylene groups, is about 94° (111). Therefore, if the oxidized molecules formed a coherent structure with an outermost surface composed entirely of the methylene or methyl groups of the hydrocarbon chain, the contact angle should approach 90° when the monolayer was completely oxidized. The relatively low contact angle indicates that the hydrophilic oxygen groups formed during autoxidation were accessible to the water. The exposure of the oxygen groups might occur if there was scission of the hydrocarbon chain which is known to happen during the autoxidation of bulk systems (78).

The autoxidation of the monolayer was never complete even though aging was continued for as long as 190 hours. Aging was not usually continued for a longer time because the excessive loss of material prevented an accurate analysis of the degree of autoxidation. The maximum amount of autoxidation was about 65% of a

monolayer. This maximum can seemingly be best explained by the inability of the linoleic acid to diffuse readily on the surface. The activation energy for diffusion of fatty acids along solid surfaces at room temperature seems to be quite large (112) and may be greater than the activation energy for the reaction.* Thus, as oxidation progresses diffusion of the free radicals and the unoxidized acid may become so slow that they are effectively "frozen" in the monolayer structure in positions unfavorable for reaction. Such a situation occurs in the vinyl polymerization of undiluted monomers where the resultant polymer is above its glass temperature (113). Therefore, the reaction rate could decrease markedly and the loss of material prevents carrying the reaction on long enough to achieve complete oxidation. Thus, the fraction of the monolayer which was autoxidized could approach a maximum.

It is also possible that the maximum might be caused by the structure of the monolayer. However, this does not seem likely as will now be discussed. Honn, et al., (114) found that the rate of oxidation of ethyl linoleate adsorbed on silica gel was quite a strong function of the amount of the surface covered. When the coverage was less than a monolayer, the rate of oxidation decreased markedly. The authors attributed this to the inability of the molecules to propagate the reactions when separated by any substantial distance on the surface. If the linoleic acid exists in micellar clusters, as do solid monolayers at higher areas per molecule (115), there may be molecules between the clusters which are widely dispersed. Approximately 35% of the molecules might be dispersed sufficiently far apart to be

*Rideal and Tadayon (112) found that the activation energy for the diffusion of stearic acid over mica was about 42 kg.-cal./mole below 50°C. and about 20 kg.-cal./mole above 50°C.; the authors believed 50°C. to be the melting point of the stearic acid on the surface. In comparison, the activation energy for the autocatalyzed oxidation of ethyl linoleate is about 17.2 kg.-cal./mole (54). The activation energy for the autoxidation of linoleic acid may be even less than 17.2 kg.-cal./mole since it is more easily oxidized than the ethyl ester. Thus, it seems reasonable to expect that the rate of oxidation may be diffusion controlled.

unable to propagate the autoxidation reactions. However, the greatest possible variation in the area per molecule is from 20.5 A.^{2} per molecule* to 50 A.^{2} in order to maintain an average of 30.5 A.^{2} per molecule. The radius of a circle of 50 A.^{2} is approximately 4 A. while the distance from the surface to the double bonds is about 15 A. Thus, an area per molecule of 50 A.^{2} does not appear to be large enough to retard the propagation of the chain reaction, and the structure of the monolayer evidently does not prevent 100% oxidation of the monolayer.

Monolayers were exposed to water vapor after extensive autoxidation in the dry air had increased the contact angle to about 52°. Upon additional aging in an atmosphere of 50% relative humidity, the contact angle decreases over a fairly long period of time, as shown in Fig. 16. It was expected that there might be a small decrease due to adsorption of the water on the surface of the monolayer. However, any such decrease was expected to occur shortly after exposure of the slide. The large decrease over a long period of time indicates that the water vapor altered the oxidized portion of the monolayer. The water vapor was probably first adsorbed and then gradually diffused into the oxidized material destroying to some extent its ability to form a solid structure. As a result, the oxidized material was less able to prevent the drop of water from diffusing into the structure of the monolayer. Thus, the contact angle decreased due to the resultant increase in γ_S and the decrease in γ_{SL}.

Analysis of the Products of Autoxidation

The autoxidized portion of the monolayer was analyzed by reductive polarography and U.V. absorption in order to ascertain what types of products were formed. By

*This is the average area per molecule in a closely packed stearic acid monolayer (104).

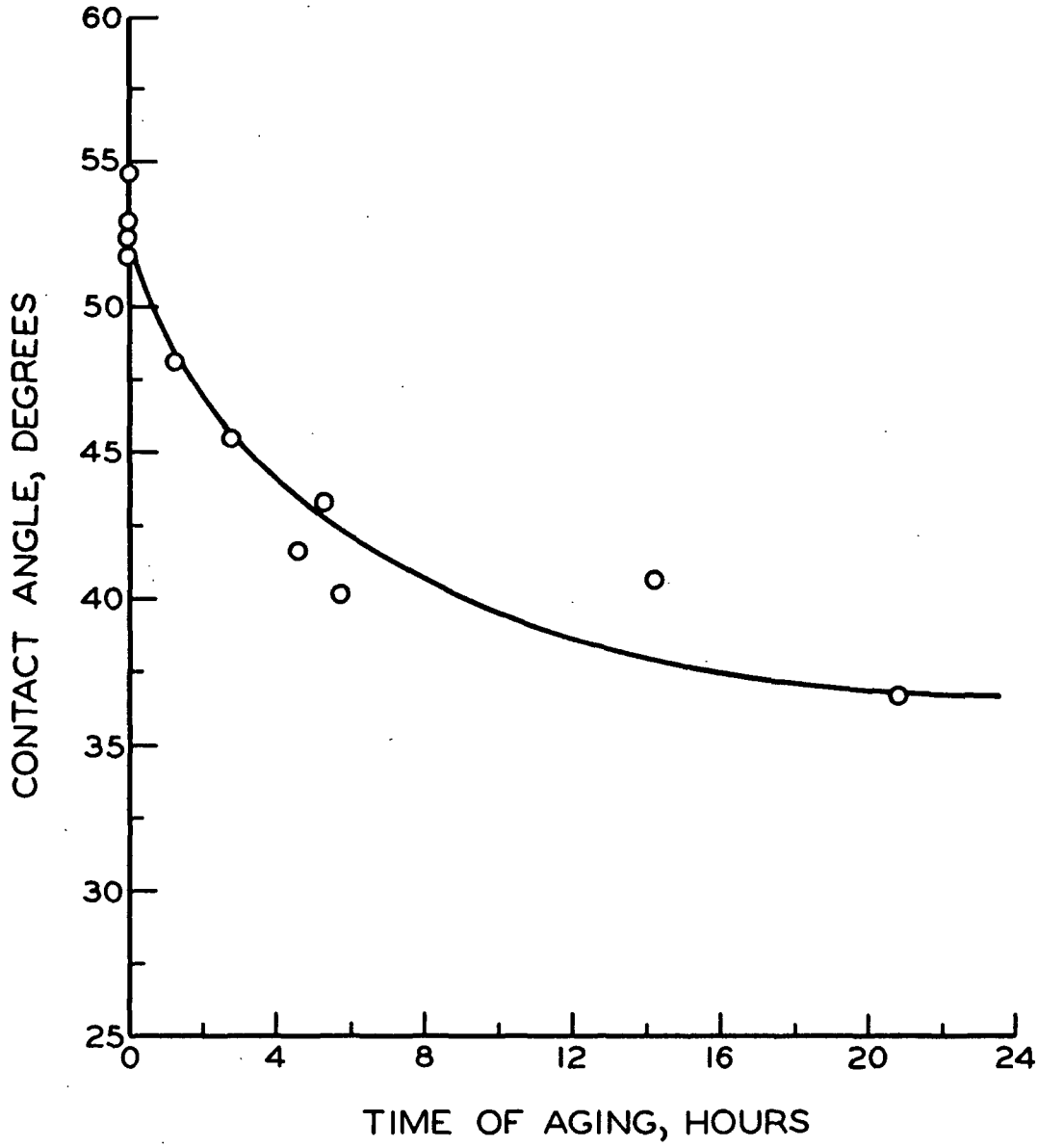

Figure 16. Decrease in the Contact Angle with Water Upon Aging of the Monolayer in Air of 50% Relative Humidity. The Initial Angle of About 53° was Obtained by First Aging the Monolayer in Dry Air

comparing the results with published data on bulk systems, information relative to the physical and chemical nature of the products was obtained.

Analysis by Polarography

The material (formed at the latter stages of autoxidation when the contact angle was about 45°) was isolated using the two methods described in the experimental procedures (see pages 54-56). The polarogram of the material isolated by the first method is shown in Fig. 17. Two reductive waves are formed. The first wave is drawn out and concentration dependent, indicating that the reduction was irreversible. The half-wave potential is -1.03 volts. The second wave is highly distorted (the peak is not shown) and this prevented an accurate determination of the half-wave potential. However, it appeared to be about -1.3 volts. The polarogram of the material isolated by the second method is shown in Fig. 18. In addition to the above-mentioned waves,* an additional wave with a half-wave potential at -0.28 volt is obtained. Also, there is a fourth wave with a half-wave potential of -1.70 volts which, however, is close to the decomposition potential of the supporting electrolyte and therefore may have been an artifact.

The material formed by autoxidation became less soluble in the supporting electrolyte as the monolayer became more fully oxidized, and, therefore, the material formed in the early stages of oxidation was also isolated. The average contact angle between water and these monolayers was about 33°. Only that part of the oxidized material which was removed by the supporting electrolyte without the

*The half-wave potentials of the second and third waves in Fig. 18 are more negative (-1.10 volts for the second wave and about -1.40 volts for the third) than the comparable waves in Fig. 17. However, as the solution was made more dilute the half-wave potentials of the second and third waves became more positive and were closer to the half-wave potentials of the comparable waves shown in Fig. 17.

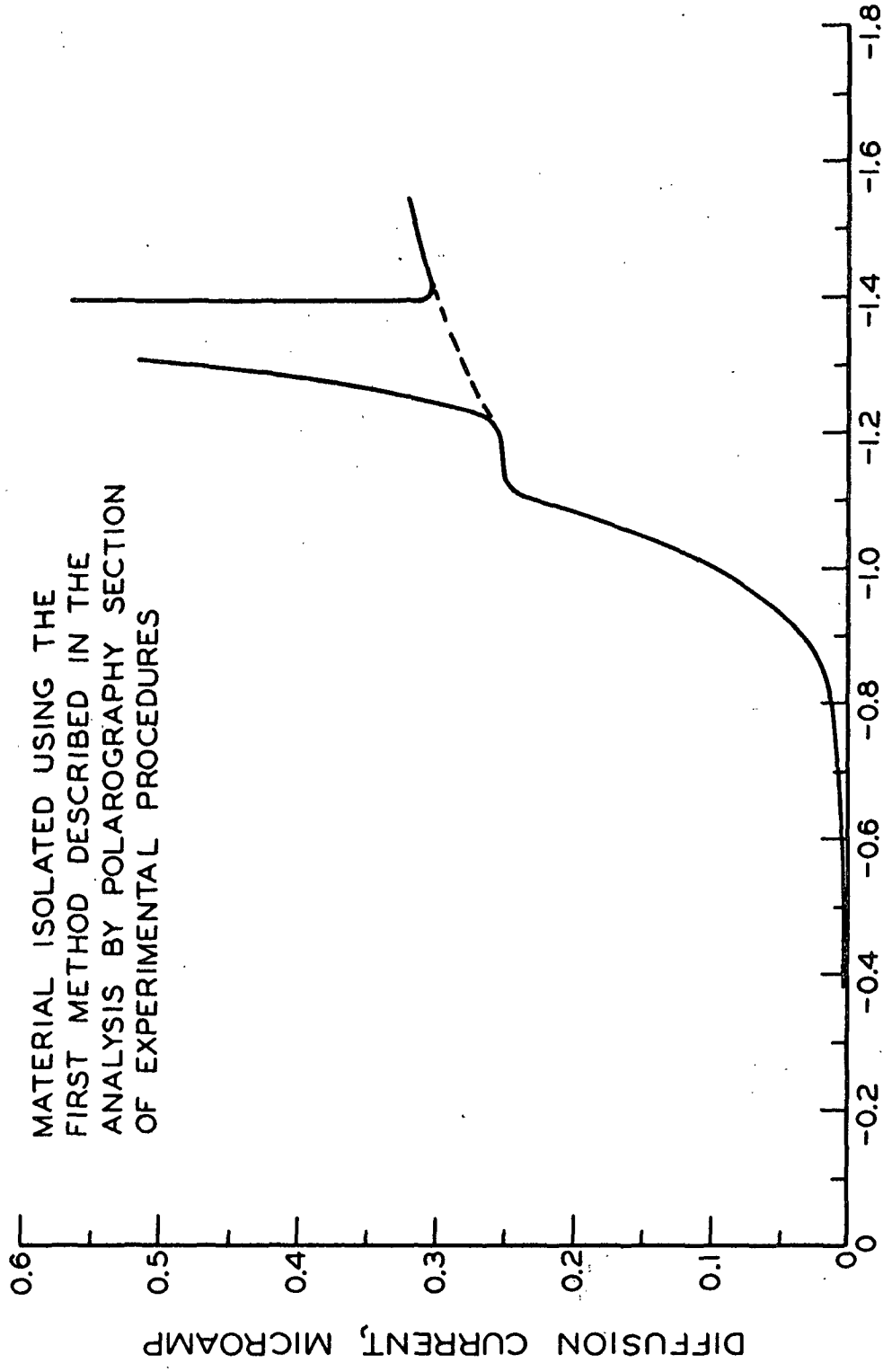

Figure 17. Polarogram of the Material Formed After Extensive Autoxidation of the Monolayer in Dry Air

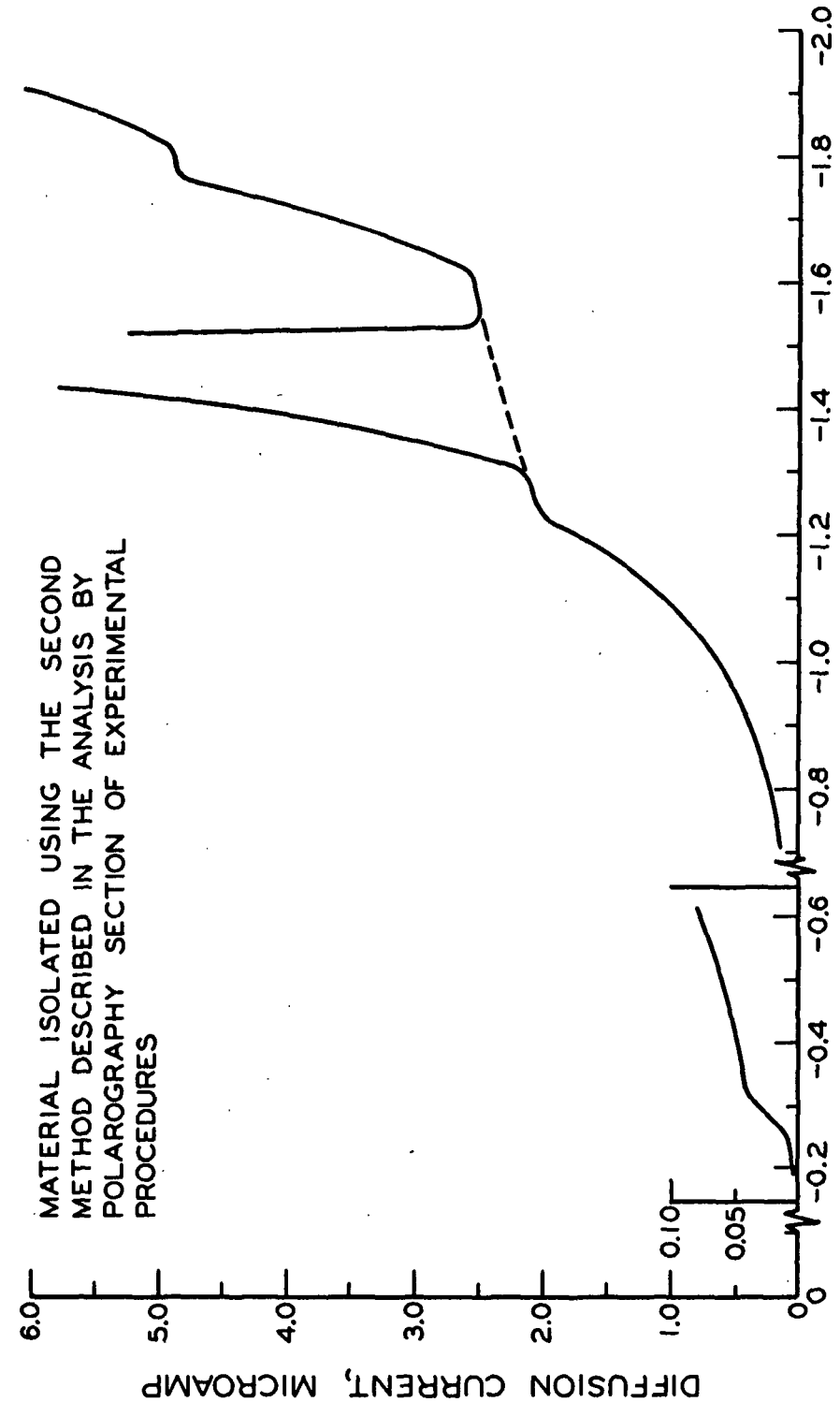

Figure 18. Polarogram of the Material Formed After Extensive Autoxidation of the Monolayer in Dry Air

benefit of mechanical abrasion was analyzed. The polarogram of this material is shown in Fig. 19. A reductive wave with a half-wave potential of -0.3 volt is obtained. It was probably due to the reduction of the same material which reduced at -0.28 volt in the previous analysis. The irreversible wave with a half-wave potential between -1.03 and -1.10 volts is absent. A small distorted wave at about -1.33 volts is obtained, but its height is much less than the corresponding wave obtained in the analysis of the highly oxidized material. The data indicate that the more insoluble material was associated with these latter two waves and that more of this material was formed as autoxidation became more extensive.

The autoxidation of unsaturated fatty acids and their esters in bulk systems produces material which gives reductive waves similar to those formed by the oxidized monolayer. Also, the half-wave potentials of the reductive waves were more a function of the conditions of oxidation than the molecular structure of the unoxidized acid or ester. A number of authors have found that oxidized fats give a reductive wave between -0.20 and -0.30 volt. Lewis, et al., (116)* polarographically analyzed the autoxidation products of methyl oleate, methyl linoleate, and lard and found that all three gave a wave at about -0.25 volt. The authors attributed the wave to the reduction of a peroxide. Kalbag, et al., (117) analyzed the oxidation products of the methyl esters and triglycerides of soybean oil and also found that material was formed which reduced at -0.2 volt. This was also attributed to an unknown peroxide. However, these workers partially fractionated the oxidized material with Skellysolve F and acetone, and found that the material which reduced at -0.2 volt was associated with the more highly polymerized fractions. Willits, et al., (118) found that, in general, diacyl peroxides such as

*In all of the studies referred to, the authors used the same supporting electrolyte used in this study.

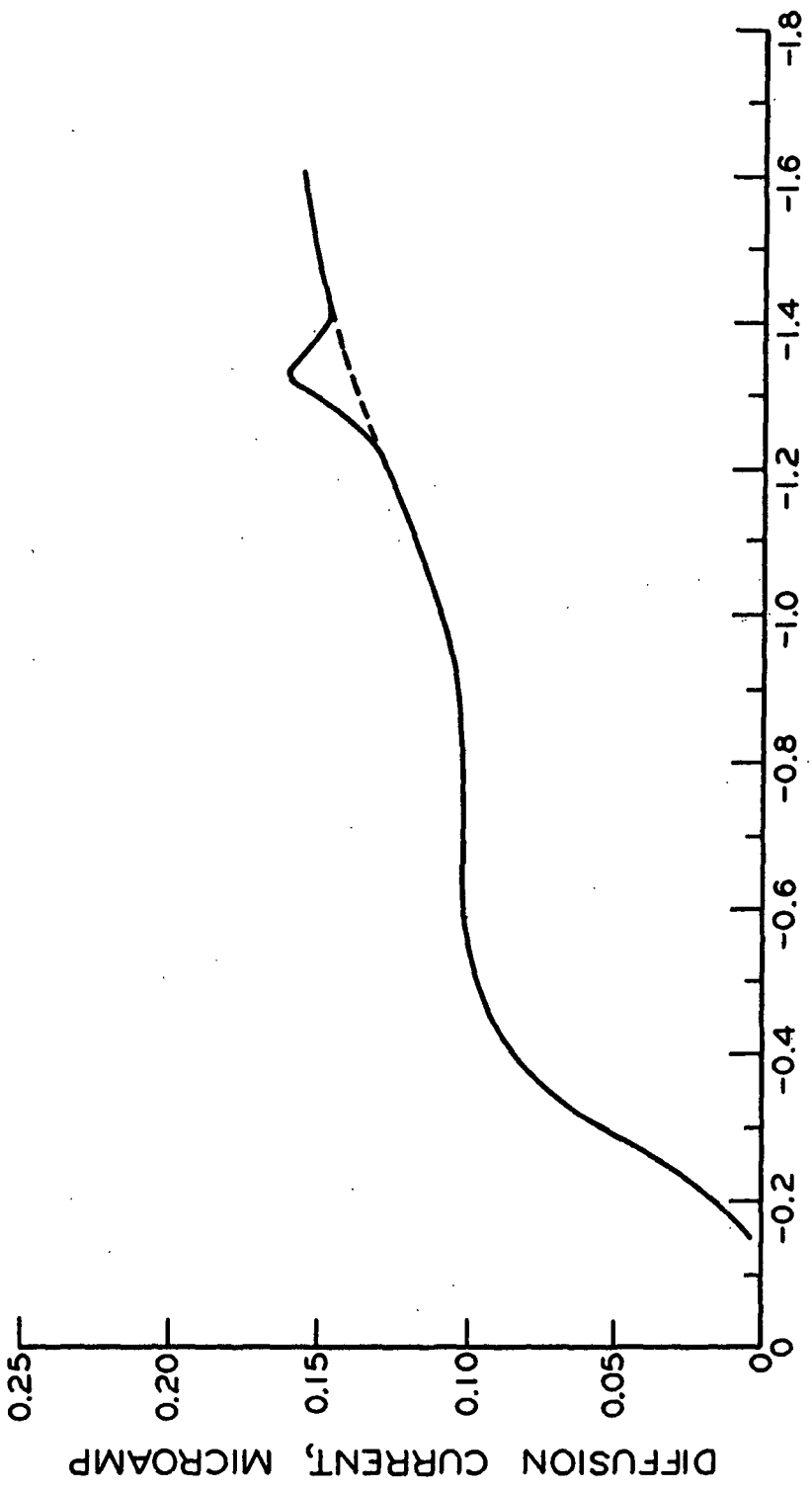

Figure 19. Polarogram of the Material Formed in the Early Stages of Autoxidation of the Monolayer in Dry Air

succinic acid peroxide were reduced at low negative potentials. Thus, the oxidized monolayer material which gave a reductive wave at about -0.28 volt was probably a peroxide and it may have been "polymeric"* in nature.

Oxidation of fats in bulk systems also produces products which are characterized by a reductive wave with a half-wave potential of about -1.0 volt. Lewis, et al., (116) found that when lard was extensively autoxidized at 100°C. the reductive waves characteristic of the initial products, including the one at -.25 volt, were no longer evident. Instead an irreversible wave appeared in the region of -1.0 volt. Schauenstein, et al., (119) oxidized ethyl linoleate in a water emulsion for 10 days and analyzed the products extractable with chloroform. The material exhibited reductive waves with half-wave potentials of -1.0 and -1.45 volts. The material with a half-wave potential of -1.0 volt was identified as a lipid hydroperoxide through the use of infrared spectra and chemical analyses. Finally, Kahn (120) analyzed the solid peroxides from the volatile products produced during the autoxidation of methyl oleate. The solid peroxides were reduced at a half-wave potential of about -1.0 volt. The wave was irreversible and very drawn out. An almost identical wave was formed by the reduction of methyl amyl ketone peroxide and hydroxy heptyl peroxide. The solid peroxide from the linoleate also gave a very similar wave. Kahn considered the products formed from both the oleate and linoleate to be peroxides of the carbonyl type, polymeric in nature but not specifically identified. Therefore, the monolayer material which reduced at a half-wave potential between -1.0 and -1.1 volts can probably best be described as a lipid hydroperoxide, which, in addition, may contain a carbonyl group. Also, it is probably a polymeric solid.

*The term "polymeric" when used in regard to the products of fat autoxidation refers to relatively low molecular weight material such as dimers or, at the most, trimers.

Oxidation products which exhibited reductive waves with half-wave potentials between -1.0 and -2.0 volts are usually characterized as being ketones or aldehydes conjugated with carbon-to-carbon double bonds (118). Schauenstein, et al., (119) found that about 25% of the chloroform-extractable material formed during the oxidation of ethyl linoleate exhibited a wave whose half-wave potential was -1.45 volts. The authors characterized the structure using U.V. and I.R. spectra and chemical analyses, and attributed the wave to the reduction of a -CH=CH-COOR structure. Thus, the distorted wave at about -1.3 to -1.4 volts and the wave at -1.7 volts were possibly due to the reduction of similar structures which contained carbonyl groups.

In summary, the polarographic data indicate that the autoxidation of the monolayer produced products which were similar to those produced in the oxidation of bulk systems. Much of the material probably consisted of solid peroxides of hydroperoxides and some evidence for carbonyl groups was obtained. Significantly, no evidence was obtained for the initial 9 or 13-hydroperoxide which reduces from -0.8 to -0.9 volt (116, 117, 121). Undoubtedly, the oxidized material consists of secondary oxidation products arising from the breakdown of the initial hydroperoxide.

Analysis by U.V. Absorption

The U.V. spectrum of the oxidized material was determined in neutral and alkaline methanol. The monolayers which were analyzed exhibited a large contact angle with water and therefore were quite highly oxidized. The spectrum in the neutral methanol does not exhibit any definite bands although a plateau is present in the wavelength region from 260 to 280 mμ as shown in Fig. 20. In alkaline methanol the absorption is increased at all wavelengths which indicates the presence of enolizable substances.

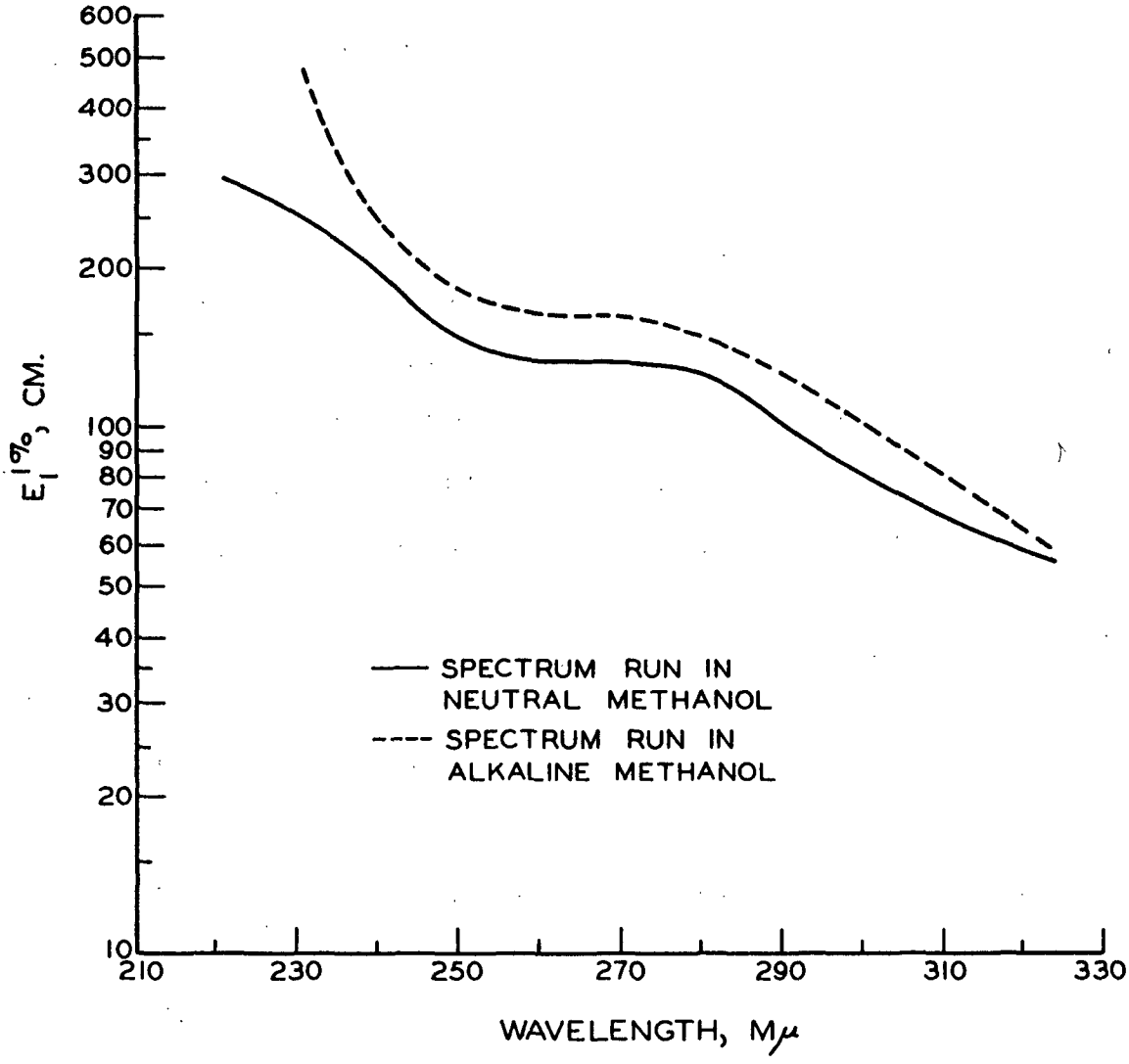

Figure 20. U.V. Spectra of the Monolayer Material After Autoxidation of the Monolayer in Dry Air

The air oxidation of linoleic acid in bulk systems produces a marked increase in the absorption at about 232 mμ due to the conjugation of the double bond during the formation of the initial hydroperoxide, as shown by Holman, et al., (122). However, the oxidation of conjugated linoleic acid resulted in a marked decrease in the absorption at about 232 mμ indicating that conjugation was destroyed. Thus, at longer times of oxidation the rate of destruction could exceed the rate of formation of conjugated systems and the reaction products could exhibit little diene conjugation. Holman also found that the oxidation of both the conjugated and unconjugated acid produces a general increase in the absorption beyond 250 mμ. A particularly strong band appeared at about 275 mμ which increased in intensity when the spectra were run in alkaline alcohol, and, thus, it was due partly to enolizable substances. Actually, the entire spectrum beyond 250 mμ increased in intensity when the oxidized linoleic acid was run in alkaline methanol, indicating that the oxidation reactions lead to a variety of enolizable products.

Hendrickson, et al., (123) studied the U.V. spectra of the products of autoxidation of linseed oil films containing mostly the esters of oleic, linoleic, and linolenic acids. These authors found that the absorption in neutral methanol at 240 mμ* and at about 270 mμ was characteristic of the secondary oxidation products formed in the early stages. As oxidation continued these bands disappeared indicating a large loss in diene conjugation and also carbonyl conjugation. The authors described the film as "dry to touch" when the above bands were at their maximum and as "hard with no tack" after oxidation had occurred to the point at which the above specific absorption bands were absent. However, even after

*The authors failed to carry the spectra to wavelengths low enough to observe the peak at 232 mμ which is characteristic of diene conjugation. Therefore, they used 240 mμ as indicative of absorption due to this chromophore.

extensive autoxidation the spectra when run in alkaline methanol increased generally over the whole wavelength range, especially at about 275 to 280 mμ and also at 370 mμ. Thus, there was still some enolizable material present after extensive autoxidation.

Recently Helmer, et al., (124) confirmed these findings. The authors oxidized linseed oil esters in the bottom of petri dishes in films about 3 mm. thick at 30°C. After extensive autoxidation (in excess of 500 hours for films aged in the absence of light), the course of oxidation was typified by decomposition of the hydroperoxides and secondary oxidation products to form scission products and polymers. During this period the optical densities of methanol solutions of the material decreased markedly at 232 and 270 mμ. The U.V. spectra in the latter stages of oxidation showed no definite bands but only a general increase in absorption over the whole U.V. spectrum.

Thus, the U.V. spectra of the oxidized monolayer were quite similar to those of films of unsaturated fatty acid esters which were highly oxidized and in a solid state. The absence of specific bands and a general absorption over the whole spectrum indicates that the monolayer material was highly oxidized and may have been in a solid state.

In summary, the analysis of the oxidation products tends to confirm the hypotheses arrived at from the contact angle data. The products of oxidation were evidently comparable in many respects to those produced in highly oxidized bulk systems. From the nature of the products, it seems likely that they were capable of forming a solid, coherent-type structure which could prevent the water from diffusing into the oxidized part of the monolayer while the periphery of the drop was advancing over the monolayer surface. Also, it appears that the oxidation products were quite heterogeneous and that they were more highly oxidized in the

later stages when more of the monolayer was autoxidized. Furthermore, oxidation seems to have progressed to the point where scission of the linoleic acid molecules at the double bond could have occurred. Thus, oxygen groups may have been in positions which were readily accessible to the water. This may explain why the contact angle obtained by extrapolation to complete oxidation was less than expected.

Contact Angle Between Methylene Iodide and the Autoxidized Monolayer

The contact angle between methylene iodide and the autoxidized monolayer was studied because the methylene iodide molecule is much larger than the water molecule and exhibits little affinity for the glass surface.* The cosine of the angle between the methylene iodide and the monolayer is not greatly affected by autoxidation, as shown by the relationship between cosine θ and the amount of autoxidation in Fig. 21. The contact angle obtained by extrapolating to zero oxidation was about 43° which was somewhat lower than the contact angle against polyethylene which is 52° (111). However, the angle obtained by extrapolating to complete oxidation was 47° which indicates that autoxidation does increase the contact angle slightly. Removal of the unoxidized linoleic acid from the monolayer has little effect on the cosine of the contact angle when the oxidized material amounts to more than 40% of a monolayer as shown in Fig. 22. However, when the oxidized material amounts to less than 40% of a monolayer, the cosine begins to decrease. The curve appeared to extrapolate to about 0.866 (contact angle of 30°) at zero per cent of a monolayer which is about the cosine of the angle between methylene iodide and a clean glass surface. Diffusion of the methylene iodide into the

*The contact angle between a clean glass slide and the methylene iodide, whose surface tension is 50.8 dynes per cm. at 20°C. (16), was 30 degrees. The relatively large angle shows that the methylene iodide has little affinity for the glass.

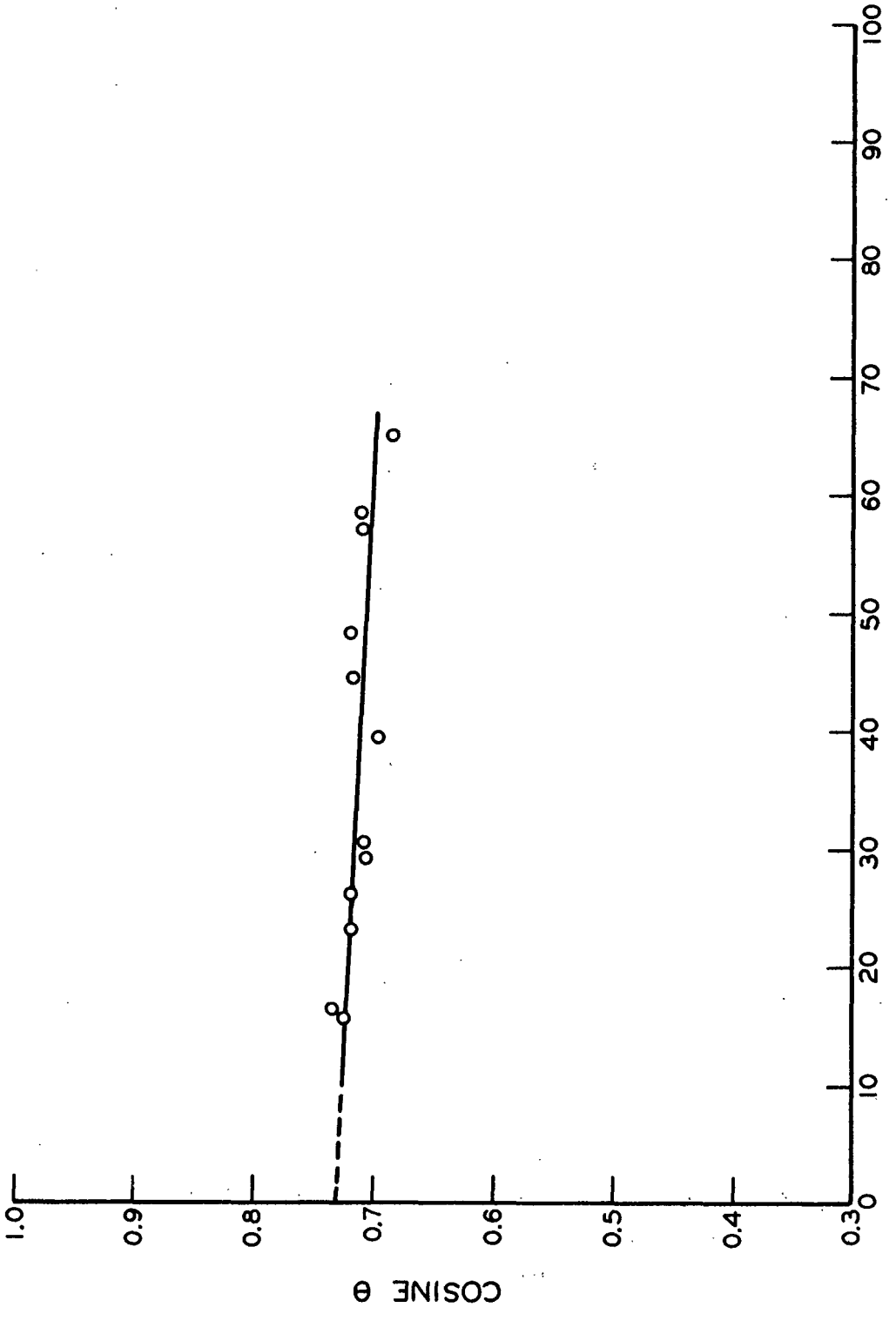

Figure 21. Cosine of the Contact Angle With Methylene Iodide as a Function of the Amount of the Monolayer Autoxidized

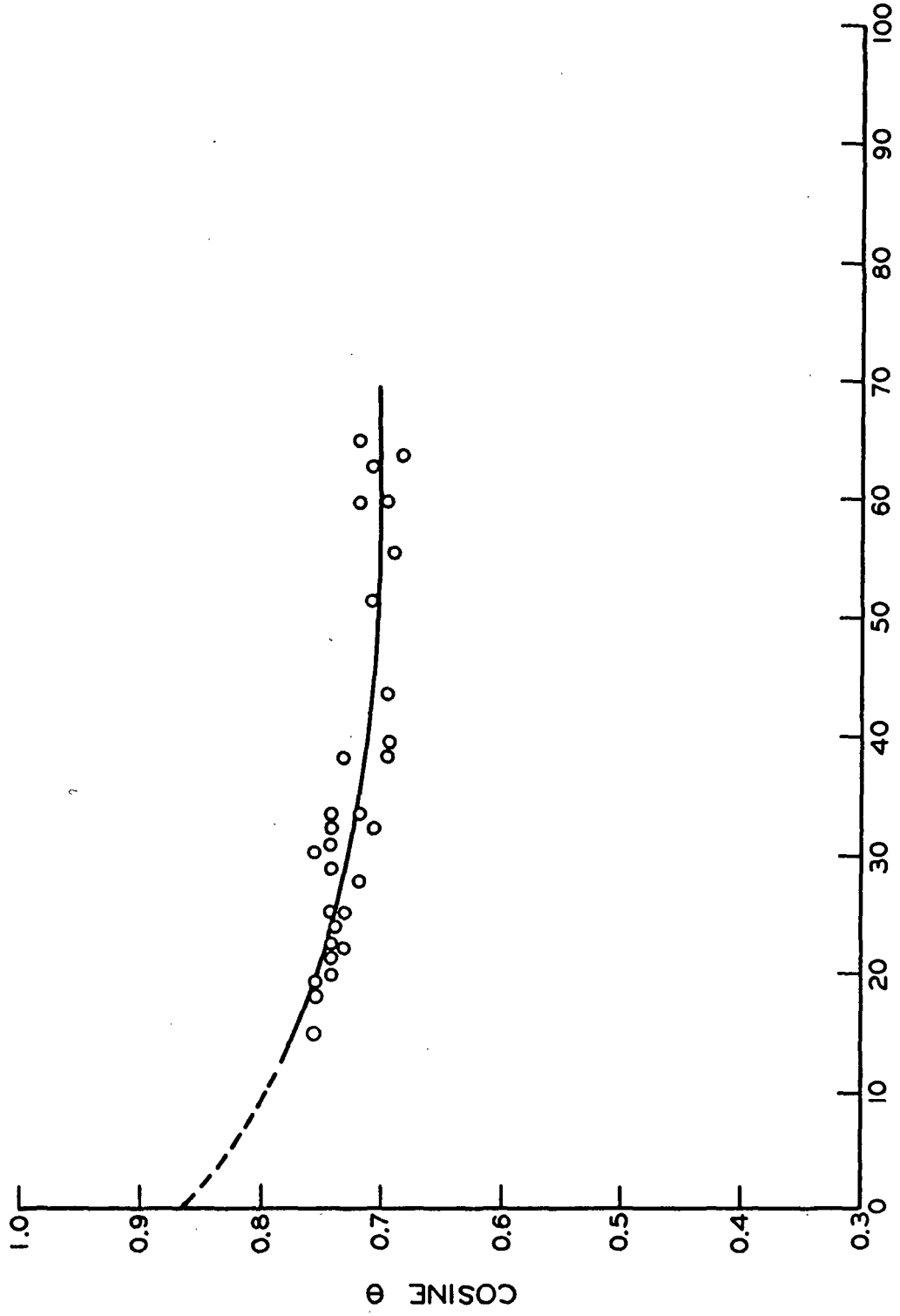

Figure 22. Cosine of the Contact Angle Between Methylene Iodide and the Products of Oxidation as a Function of Surface Coverage

monolayer was probably greatly reduced because the methylene iodide molecule is quite large. Also, the low attraction of the methylene iodide for the glass relative to the attraction between the carboxyl group and the glass probably prevented the methylene iodide from diffusing along the monolayer-glass interface. Thus, diffusion of the methylene iodide outside the drop periphery was greatly reduced and the effective free surface energy of the monolayer at the drop boundary may have approached that of the hydrocarbon chains. As a result, the cosine of the contact angle was influenced less by the motion of the unoxidized acid and by depletion of the monolayer. In contrast with water, changes in the cosine of the contact angle were probably associated more with changes in $\gamma_{\underline{SL}}$ rather than $\gamma_{\underline{S}}$.

The specific interfacial free surface energy, $\gamma_{\underline{SL}}$, can change during autoxidation as follows: The specific interfacial energy between methylene iodide and carbon-to-carbon double bonds is lower than expected (110). When the monolayer was unoxidized, the double bonds were probably accessible to the methylene iodide due to the motion of the hydrocarbon chains. Thus, $\gamma_{\underline{SL}}$ and in turn the contact angle was lower than it would be against a hydrocarbon surface made up of only $-CH_2-$ and $-CH_3$ groups. As autoxidation occurred and the motion of the hydrocarbon chains decreased, the double bonds probably became less accessible to the methylene iodide. As a result, $\gamma_{\underline{SL}}$ would tend to increase causing an increase in the contact angle. However, the introduction of polar oxygen groups into the monolayer surface would partially offset any increase in $\gamma_{\underline{SL}}$ caused by removing carbon-to-carbon double bonds from the surface. Undoubtedly, this competing effect limited the magnitude of the change in $\gamma_{\underline{SL}}$ so that a large change in the cosine of the angle was not obtained.

Summary

The contact angle between water and the unoxidized linoleic acid was zero irrespective of its concentration in the monolayer. Apparently, a stable boundary

between the hydrocarbon portion of the unoxidized acid and the water was not formed because the acid was in the liquid state and because the attraction of the water and the carboxyl group for the glass surface were nearly the same. As a result, the water was evidently able to diffuse rapidly into the unoxidized monolayer which presumably increased the specific free surface energy of the monolayer until it was nearly that of the water. Therefore, the contact angle was zero. However, autoxidation of the monolayer in dry air produces material which increases the contact angle with water. Analysis by polarography and U.V. absorption indicated that the oxidized material was similar to solid oxidation products produced in bulk systems. The more coherent structure formed upon autoxidation evidently prevented the water from diffusing into the oxidized part of the monolayer, and, therefore, the contact angle increased (cosine θ decreased) upon autoxidation. The magnitude of the increase is limited by incomplete oxidation. The increase was also limited apparently by the presence of oxygen groups in the outermost surface of the monolayer since upon extrapolation to complete autoxidation the contact angle was only 71°. Exposure of the highly oxidized monolayer to water vapor results in a decrease in the contact angle. Evidently, the water vapor altered the oxidized portion of the monolayer in such a manner that it was less able to increase the contact angle with the water. Probably the water vapor was first absorbed and then gradually diffused into the oxidized material destroying to some extent its ability to form a solid structure.

In contrast to the water, the contact angle between methylene iodide and the monolayer was not greatly affected by autoxidation. Evidently, the methylene iodide did not diffuse into the monolayer because the molecule was quite large and because it had little attraction for the glass surface. Thus, the contact angle was apparently less influenced by the motion of the unoxidized linoleic acid molecules and therefore was less influenced by changes occurring during autoxidation.

AUTOXIDATION IN THE PRESENCE OF WATER VAPOR

Rate of Autoxidation

The rate of autoxidation in air at 50% relative humidity was more reproducible than in dry air. Thus, a limited amount of rate data was taken to determine whether the per cent of the monolayer which was autoxidized approached a maximum. As usual, the per cent oxidation was determined by hexane solubility and by chromatography. However, the hexane solubility method failed to give a good measure of the per cent oxidation because the separation of the oxidized and unoxidized materials was incomplete. A large amount of the unoxidized linoleic acid was retained in the monolayer and as autoxidation progressed apparently about one unoxidized linoleic acid molecule was retained for every oxidized molecule (see Fig. 23).* However, apparently the retention of the unoxidized acid was not simply due to the increased concentration of water in the monolayer. Immediately after deposition, analyses by the two methods were in good agreement, and at that time the monolayer contained at least as much water as it would after coming to equilibrium with the air at 50% R.H. Thus, there may be an association between the oxidized and unoxidized molecules which was participated in by the water, and the distribution of the water in the monolayer was the more important factor in preventing the hexane from making a clean separation.

*The assumption was made that the chromatographic data were more reliable in this instance. The value obtained with chromatography could possibly be greater than the value obtained by hexane insolubility due to autoxidation during the time required for chromatographic separation. However, the much lower value obtained with chromatography could seemingly only arise if a considerable portion of the oxidized material moved at the same rate as the unoxidized linoleic acid. This seems unlikely and therefore the chromatographic analysis was considered more reliable.

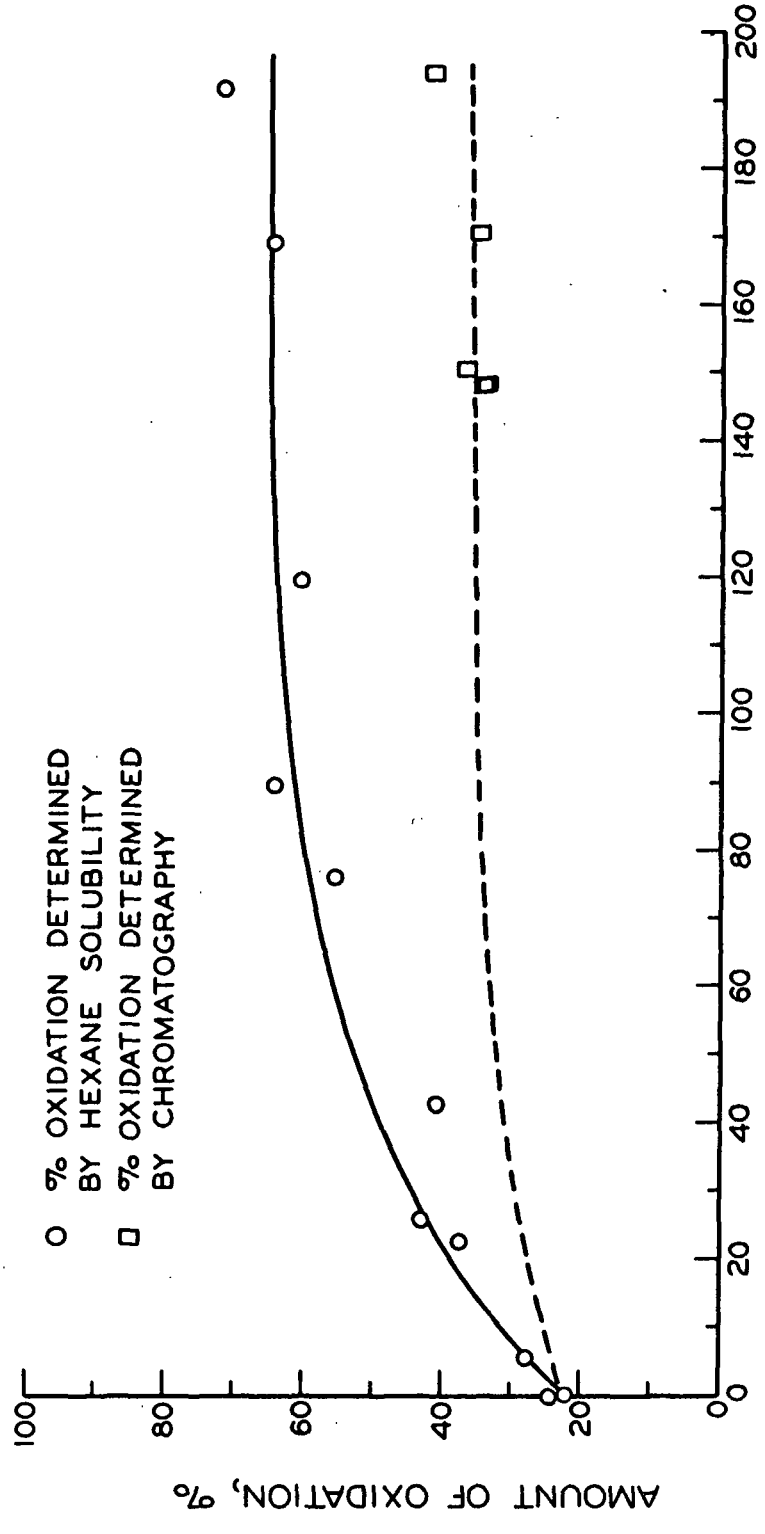

Figure 23. Amount of Oxidation of the Monolayer as a Function of the Time of Aging in an Air Atmosphere of 50% Relative Humidity

It is evident from the relationship in Fig. 23 that the amount of the monolayer which was autoxidized seemingly approached a maximum. Chromatographic analyses indicated that this was about 35%. The reasons for the apparent maximum were probably the same as when the monolayer was aged in the absence of water vapor. However, the maximum amount of autoxidation was apparently about one half of that obtained in the dry atmosphere. Possibly an oxidized molecule prevents the autoxidation of a neighboring molecule through an association involving the water and the double bonds of the unoxidized molecules. The maximum amount of oxidation could then conceivably be about half that obtained in the absence of the water vapor.

Aging of the monolayers in nitrogen of 50% R.H. decreases the rate of autoxidation as indicated by the decrease in hexane solubility with time (see Fig. 24). However, the maximum amount of oxidation may be nearly the same as when the monolayers were aged in air. It was impossible to prevent autoxidation because trace amounts of oxygen in the nitrogen would be sufficient to oxidize the monolayer.

Contact Angle Between Water and the Autoxidized Monolayer

The contact angle with water did not increase upon autoxidation even after aging for 191 hours as shown by the data in Table XIII.* Conceivably, the presence of water could have prevented the oxidation products from forming a solid structure without materially altering the course of the autoxidation. To check this possibility, monolayer number 95-5 was aged for about 214 hours in the presence of water vapor and then transferred to dry air where the aging process was continued. The

*Admittedly, the monolayer was probably oxidized only 35% after 191 hours of aging. However, the lack of a contact angle increase cannot be attributed to the lack of sufficient oxidation because when the monolayer was oxidized 35% in dry air the contact angle was about 35 degrees.

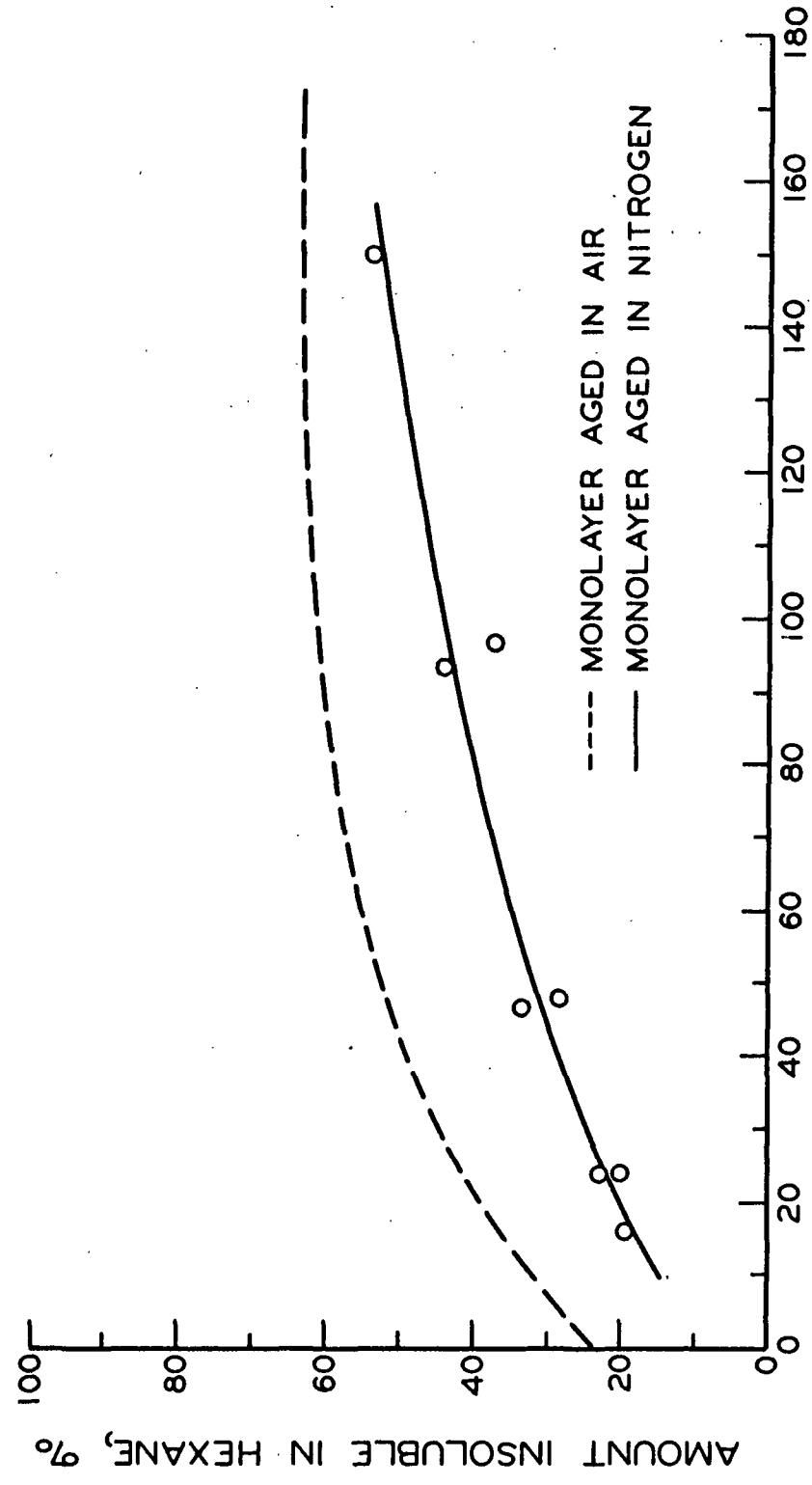

Figure 24. The Amount of the Monolayer Insolubie in Hexane as a Function of the Time of Aging Under Nitrogen

TABLE XIII

THE CONTACT ANGLE BETWEEN WATER AND A MONOLAYER AGED IN THE PRESENCE OF WATER VAPOR

Monolayer No.	Time of Aging, hours	Contact Angle, degrees
83-6	0.0	10
82-1	5.8	10
83-1	22.6	10
82-2	26.1	10
82-3	42.8	11
83-2	76.2	10
82-4	89.5	16
83-3	119.6	10
83-4	169.0	10
83-5	191.4	11

contact angle after aging in the presence of moisture was less than 10° and the angle did not increase until after about 21 hours of additional aging in the dry atmosphere (see Table XIV). Thus, removal of the water from the monolayer did not increase the contact angle. An increase in the contact angle was noted only after additional oxidation had time to occur in the dry air. Therefore, the data indicate that the course of the autoxidation reactions was altered by the presence of the water and that the oxidized material was apparently ineffective in preventing the diffusion of the water through the monolayer.

Analysis of the Products of Autoxidation

The analysis indicated that the products of autoxidation were quite different from those produced in dry air. The polarogram of the oxidized material is as shown in Fig. 25. Products are produced which exhibited at least three reductive

TABLE XIV

CONTACT ANGLE BETWEEN WATER AND MONOLAYER NUMBER 95-5

Time of Aging in Absence of Water Vapor, hours	Contact Angle, degrees
0.0	10
5.0	10
21.1	10
51.7	16
77.9	24
127.6	28
245.8	37

waves. The half-wave potential of the first wave is -0.22 volt, the second -0.78 volt, and the third about -1.23 volts. The first wave was probably a peroxide (116) similar to material produced by autoxidation in the dry atmosphere. The second wave was presumably due to the reduction of the 9 or 13-hydroperoxide of linoleic acid which is formed initially during autoxidation (116, 117, 121). The third wave may be due to the reduction of a carbonyl group conjugated with carbon-to-carbon unsaturation. Material which formed an irreversible wave with a half-wave potential between -1.03 and -1.1 volts was notably absent as was the distorted wave. The absence of a wave characteristic of the hydroperoxide produced after extensive oxidation and evidence for the 9 or 13-hydroperoxide of linoleic acid indicates that additional oxidation of the primary products of autoxidation had not occurred to as large an extent as in the dry air. In addition, the oxidized material was always readily soluble in absolute methanol or in a 50:50 mixture of methanol and benzene which also indicates that oxidation of the linoleic acid was less extensive.

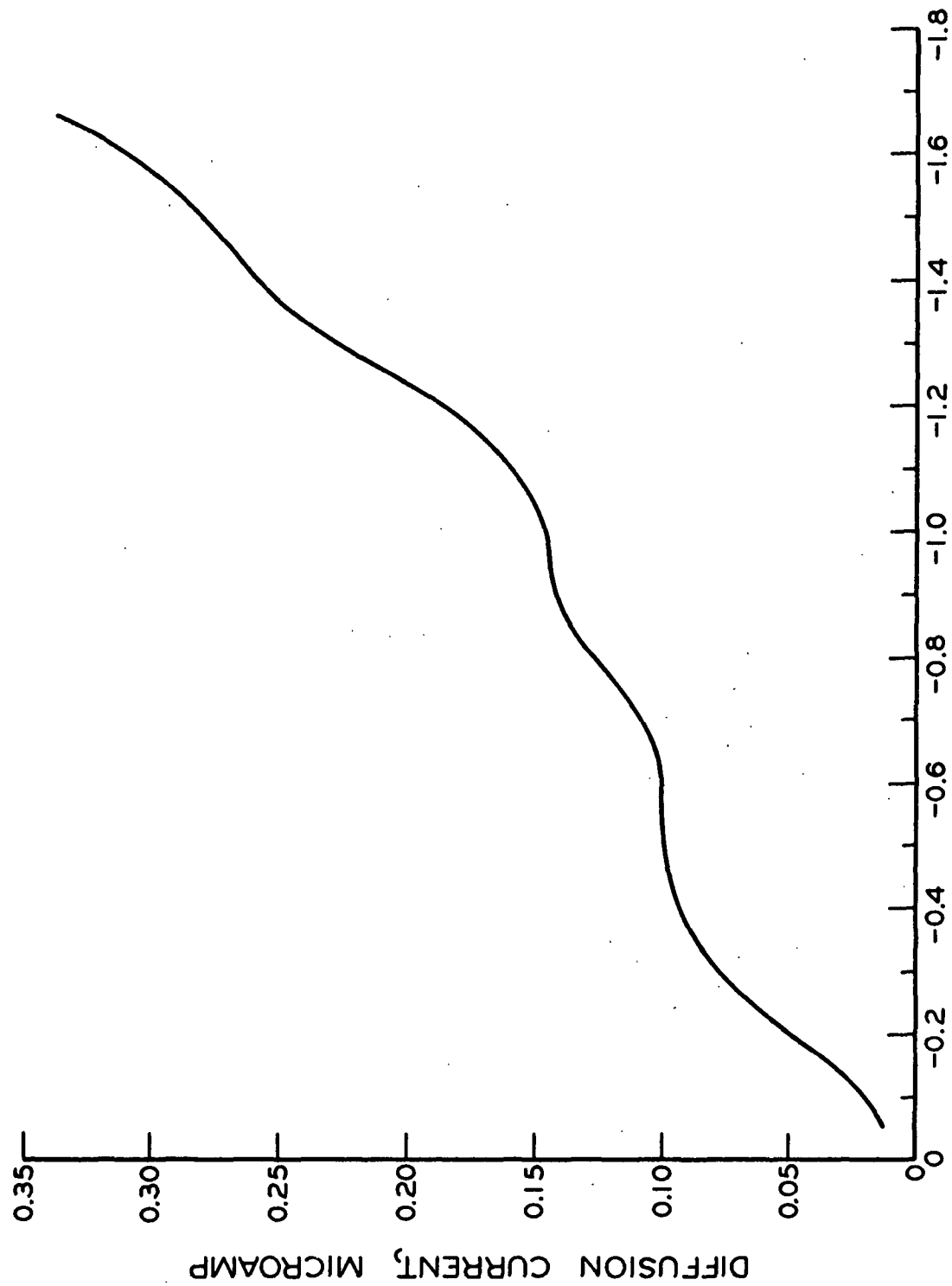

Figure 25. Polarogram of Material Formed by Autoxidation of the Monolayer in Air of 50% Relative Humidity

This conclusion was supported by the U.V. spectra, shown in Fig. 26. A band is evident at 232 mμ which indicates that a substantial number of the conjugated double bonds, which were formed during the initial step of autoxidation, had not been destroyed by additional oxidation. The peak at about 280 mμ indicates the presence of a carbonyl group conjugated with carbon-to-carbon double bonds (125). The structure of the chromophore may have been -HC=CH-HC=CH-C(=O)H- which usually absorbs in the region of 280 mμ (77). This structure could be formed by the dehydration of the 9 or 13-hydroperoxide of the linoleic acid. The decomposition of the hydroperoxide in the presence of water vapor would be expected to yield the 9 or 13-hydroxy linoleic acid (79, 80). However, Helmer, et al., (124) found that autoxidation in the absence of light favored the formation of carbonyl groups. Thus, the absence of light during the autoxidation of the monolayers probably contributed to the formation of carbonyl groups even though water was present. However, this does not preclude the possibility that a large amount of the hydroxy linoleic acid was formed since no analysis for hydroxyl groups was carried out. In general, the U.V. spectra indicates that the products of autoxidation were not as highly oxidized as when the autoxidation was carried out in the absence of water vapor. A large amount of the conjugated diene unsaturation was still present, indicating that the autoxidation was not extensive enough to form scission products and polymers.

In summary, the analysis of the products of autoxidation indicates that oxidation of the linoleic acid was not as extensive as when water vapor was absent, and that scission products and polymers were not formed in large amounts. Thus, the oxidized material was probably less capable of forming a solid, coherent-type monolayer, and as a result the contact angle did not increase.

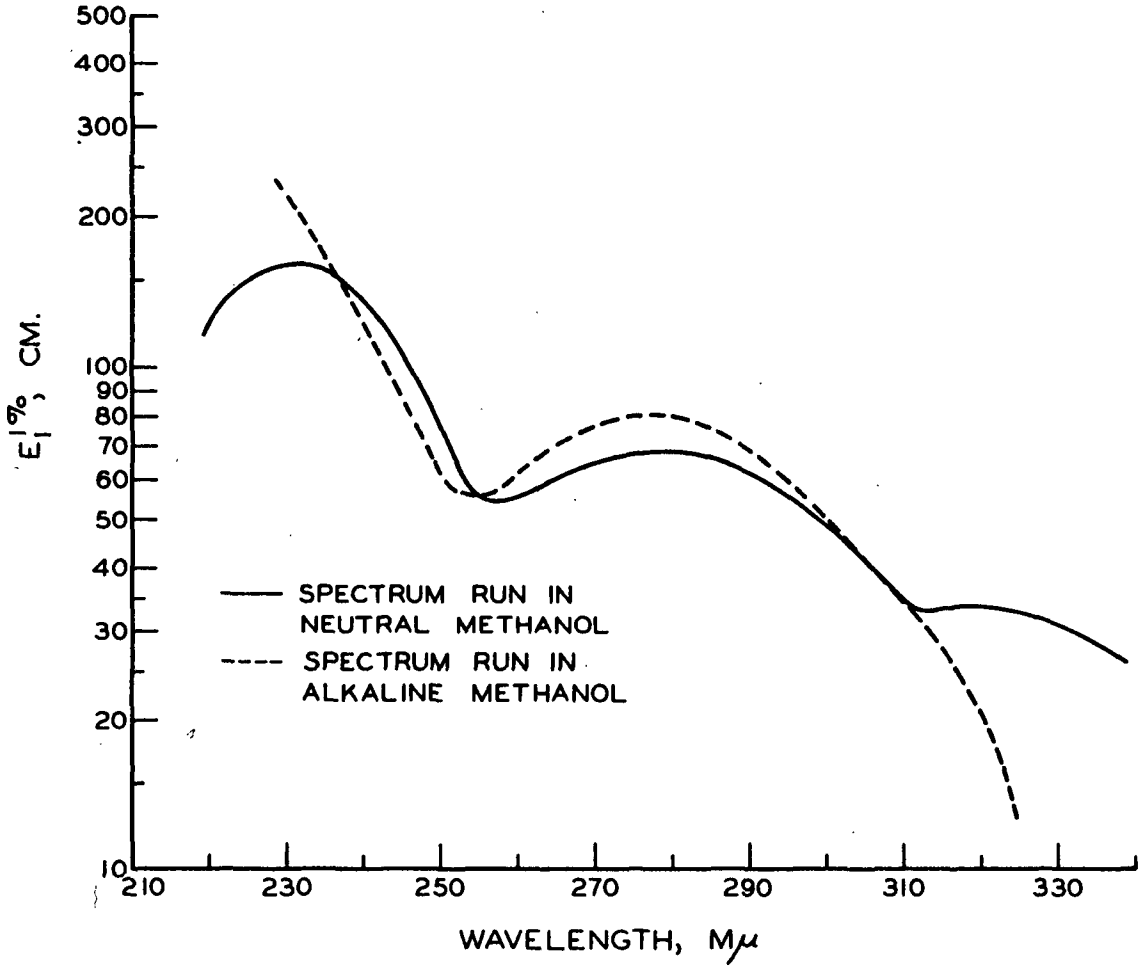

Figure 26. U.V. Spectra of the Monolayer Material After Autoxidation of the Monolayer in Air at 50% Relative Humidity

Contact Angle Between Methylene Iodide and the Autoxidized Monolayer

The contact angle between methylene iodide and the monolayer was of the same order of magnitude as when the monolayer was autoxidized in dry air. The cosine of the angle is plotted as a function of the amount of the material insoluble in hexane, as shown in Fig. 27. Hexane solubility was not a good measure of the amount of oxidation for the monolayers aged in the presence of moisture, as discussed previously. However, the decreased solubility in hexane was indicative of autoxidation and the results seem to be consistent with the other experimental data. The contact angle against the unoxidized monolayer was estimated as 44° by extrapolation to complete hexane solubility. This was comparable to the estimate obtained by extrapolation of the dry air data which was 43°. In agreement with the data obtained in the dry air, the cosine of the contact angle is not greatly affected by autoxidation. Evidently, the molecular size of the methylene iodide and the high interfacial free energy between it and the glass prevented the methylene iodide from diffusing into unoxidized portions of the monolayer, as discussed previously. However, although the decrease in the cosine of the angle is small, the decrease apparently was greater than when the monolayers were aged in dry air. The presence of moisture was less favorable to the introduction of hydrophilic groups into the monolayer surface through scission of the hydrocarbon chains. Thus, a relatively small decrease in the mobility of the oxidized acid caused a greater decrease in the cosine of the angle (or increase in the contact angle), because the specific free energy of the monolayer surface was lower.

Summary

Autoxidation of the monolayer was never complete, and apparently did not progress beyond a maximum of 35%. The data indicated that there might have been a

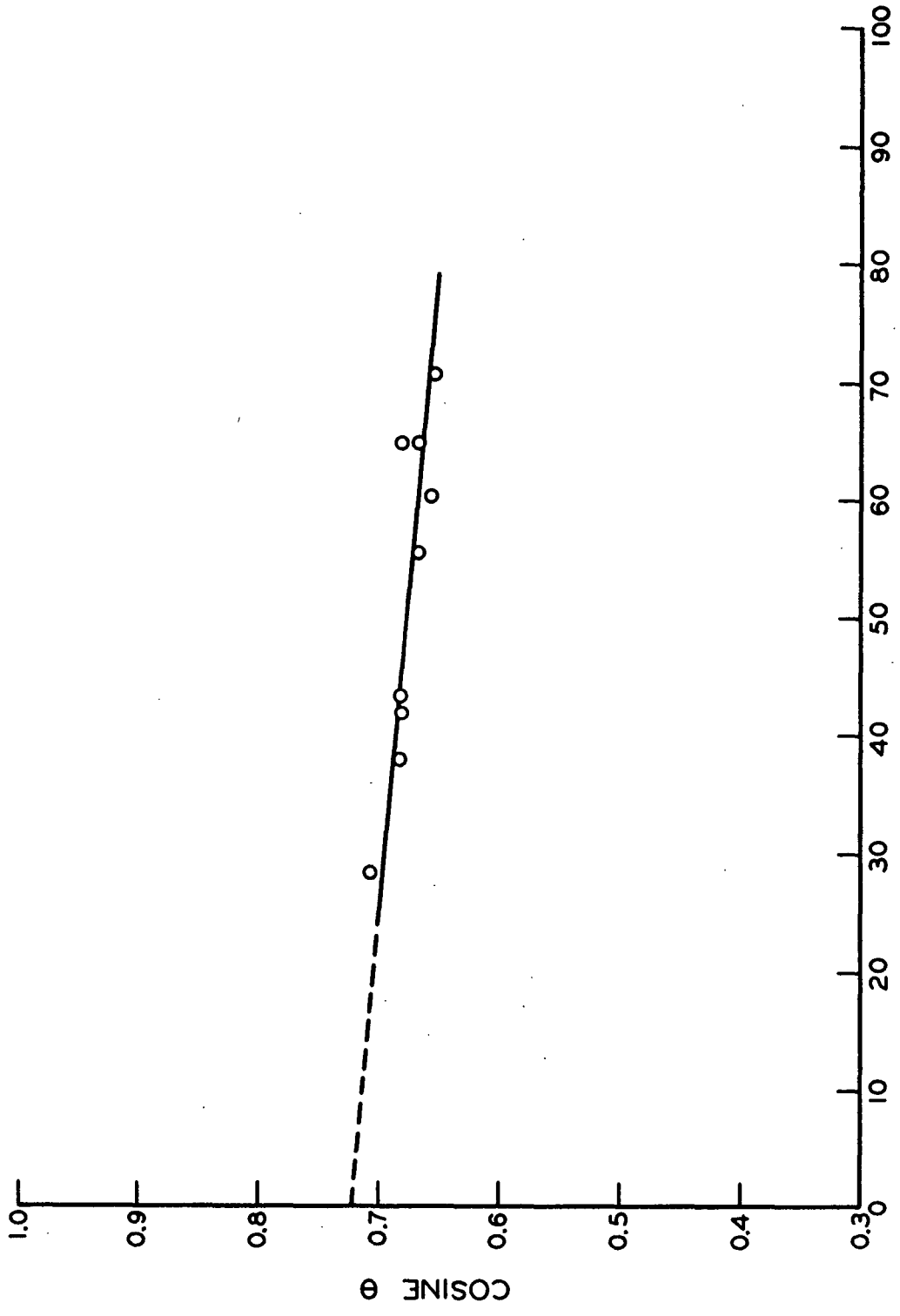

Figure 27. Cosine of the Contact Angle with Methylene Iodide as a Function of the Amount of the Monolayer Insoluble in Hexane

complex formed between the oxidized acid, the unoxidized acid, and the water which could have prevented the monolayer from autoxidizing further.

The products of autoxidation were not effective in increasing the contact angle between water and the monolayer. Analysis of the oxidized material with reductive polarography and U.V. absorption indicated that it was characteristic of material produced quite early in the oxidation of bulk systems, and that it probably would not be effective in forming a solid, coherent-type monolayer. Evidently, this was the reason the contact angle did not increase and the data was therefore consistent with the interpretation of the results of autoxidation in the dry air.

The contact angle between methylene iodide and the oxidized monolayer was of the same order of magnitude as when the monolayers were aged in the absence of water vapor. However, autoxidation in the presence of water vapor appeared tc increase the contact angle more than in dry air even though the mobility of the molecules was apparently decreased less. Possibly, the increase was greater because hydrophilic groups were not being introduced into the monolayer surface.

AUTOXIDATION OF THE MONOLAYER ON A REACTIVE SURFACE

The linoleic acid molecules were immobilized by depositing the monolayer on a copper surface with which the carboxyl group can react. Because of the increased attraction of the carboxyl group for the solid surface, the monolayer was apparently able to form a stable interface between the water and its outermost surface, and as a result the contact angle was quite high (see Fig. 28). Evidently, the reaction between the flamed copper surface and the carboxyl group was quite rapid since about 75% of the monolayer is insoluble in the hexane immediately after deposition. The resultant decrease in the mobility of the molecules was reflected in the contact

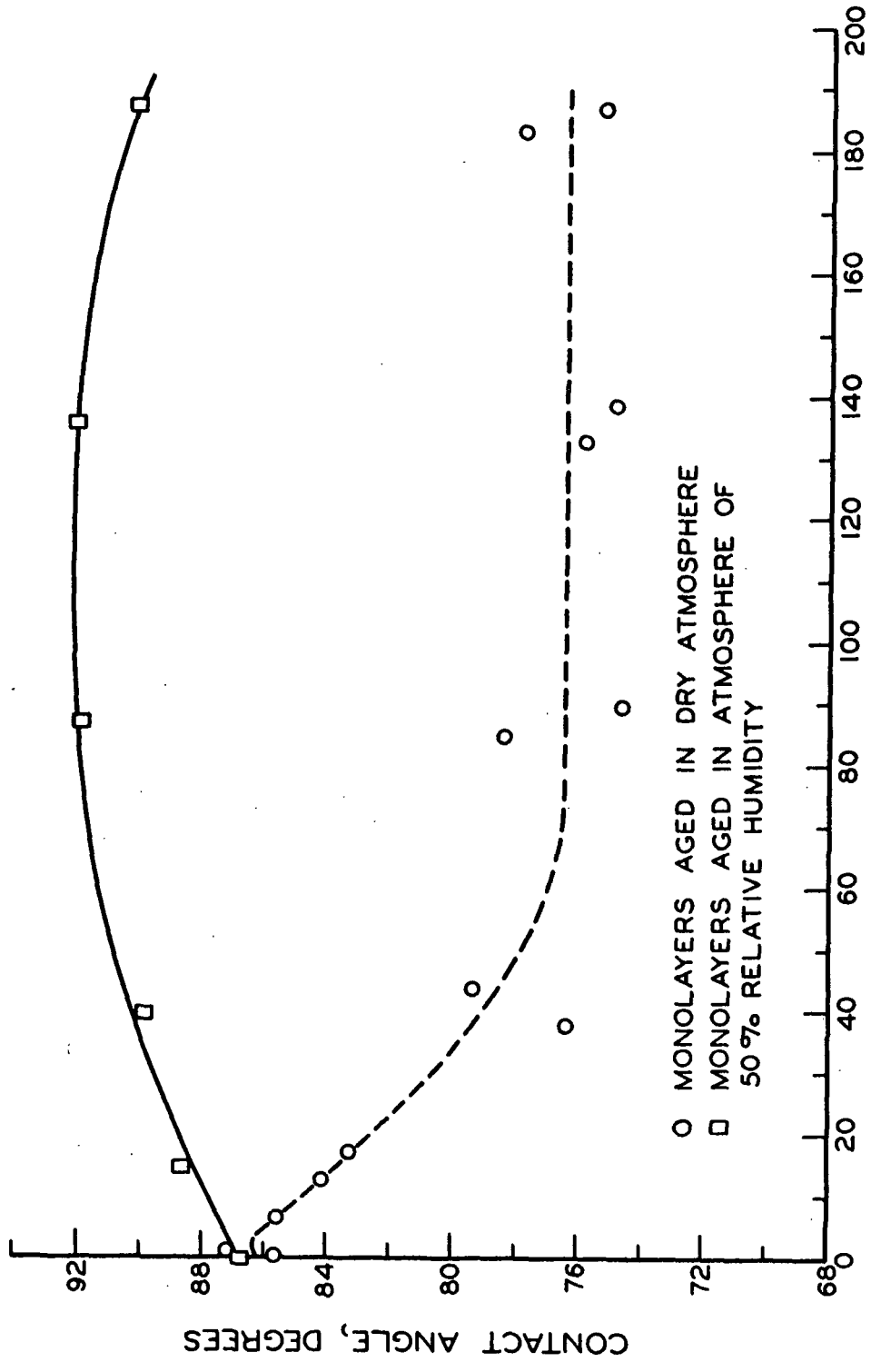

Figure 28. Contact Angle with Water as a Function of the Time of Aging of the Monolayer on a Copper Surface

angle which is about 86° directly after deposition. The monolayers were aged both in the presence and absence of water vapor as before. When the aging is carried out in the absence of moisture, the contact angle decreases from 86° to about 76.5° after about 80 hours of aging. Upon further aging the contact angle remains quite constant. In comparison, when the monolayers are aged in the presence of moisture, the contact angle increases gradually from 86 to 92° and only after extensive aging does it appear to decrease.

The copper would not be expected to alter the course of the autoxidation relative to that on the glass other than to decrease the length of the induction period and the time required to form scission products and polymers from the initial oxidation products (62). However, the formation of solid oxidation products had probably little effect on the contact angle because the molecules were already immobilized by the reaction between the carboxyl group and the copper. Instead, the location of the oxygen groups in the hydrocarbon chain was evidently the most important factor in determining changes in the contact angle. When autoxidation was carried out in the dry atmosphere, the oxygen groups were probably near the outer surface of the monolayer and accessible to the water because of scission of the hydrocarbon chain at the double bonds. Thus, as autoxidation progressed, γ_S increased and γ_{SL} decreased which resulted in a decrease in the angle.

In contrast, autoxidation in the presence of moisture was less severe and scission of the double bond probably did not occur to any extent. Thus, the oxygen groups were probably in the center of the hydrocarbon chains and less accessible to the water. Therefore, the contact angle continued to increase as more of the carboxyl groups reacted with the surface until the reaction was complete. At this point the contact angle was 92° which was comparable to the angle between water and polyethylene. However, as aging continued the contact angle apparently started to

decrease which indicated that if oxidation was continued long enough the oxygen groups might become more accessible to the water.

As stated, the contact angle decreased to a constant value when the aging was done in dry air. This may have been due to complete oxidation of the monolayer and the formation of products which were not susceptible to further oxidation. However, if oxidation was complete and the products of autoxidation were similar to those formed when the monolayer was aged on the glass surface, the minimum contact angle would be expected to be about 71° instead of about 76.5°. The larger contact angle may be accounted for by assuming that autoxidation was incomplete. The fraction of the monolayer which was autoxidized probably approached a rather reproducible maximum, thus resembling autoxidation on the glass surface. In fact, by assuming that the contact angle with just the oxidized material was the same for both the copper and glass substrates, the value of the minimum contact angle could be estimated quite accurately by Equation (36):

$$\text{cosine } \theta = (x) \text{ cosine } \theta_1 + (1-x) \text{ cosine } \theta_2. \qquad (36)$$

The maximum fraction of the monolayer autoxidized, $\underline{x}$, was assumed to be 0.65 which was the maximum amount of autoxidation on the glass surface. The contact angle against just the oxidized material, θ_1, was assumed to be 71° found by extrapolating the relationship in Fig. 14 to complete oxidation. The contact angle against the unoxidized linoleic acid, θ_2, was assumed to be 92° since the unoxidized acid when on the copper surface would present a stable low free energy surface to the water. The minimum contact angle was then calculated to be about 78° which agrees well with the experimental value of 76.5°. Thus, the final contact angle between water and the monolayer was of the magnitude expected provided autoxidation proceeded essentially as on the glass surface.

In summary, the changes in the contact angle due to autoxidation of the monolayer while on the copper surface can evidently be explained by assuming that the course of autoxidation was not greatly different than on the glass surface. They can be explained by considering the effect of immobilizing the molecules through reaction of the carboxyl group with the copper in the light of information obtained from the analysis of the products formed by autoxidation on the glass. Because the molecules were already immobilized through reaction of the carboxyl group with the copper, the formation of solid oxidation products did not increase the contact angle. Instead, the extensive oxidation which occurred upon aging in dry air resulted in a decrease in the angle apparently because hydrophilic oxygen groups were present in or near the surface of the monolayer. In contrast, when the monolayer was aged in the presence of water vapor, the oxygen groups were evidently located near the center of the hydrocarbon chains and the contact angle increased to 92° as the reaction between the carboxyl groups and the copper became complete.

SUMMARY

Autoxidation of the linoleic acid monolayer was carried out in dry air and on a glass surface with which the carboxyl group did not react. The results and their explanation were as follows:

1. The contact angle with water increased from zero degrees, when 15% of the monolayer was autoxidized, to 56 degrees, when 65% was oxidized.
2. The unoxidized linoleic acid was evidently unable to prevent the water from diffusing into the monolayer because of the mobility of the molecules. As a result, a stable interface between the unoxidized monolayer and the water was evidently not formed. Autoxidation apparently led to solid oxidation products which were capable of forming a stable interface. Therefore, the increase in the contact angle was controlled by the degree of autoxidation and by the specific free surface energy of the oxidized material.
3. The increase in the contact angle was limited by the amount of autoxidation and evidently by the introduction of hydrophilic oxygen groups near the surface of the oxidized material.
4. Analysis of the products of autoxidation with reductive polarography and U.V. absorption supported the conclusions deduced from the contact angle data. The material was comparable to solid products produced upon extensive autoxidation of bulk systems. They were undoubtedly capable of forming a solid-coherent structure which could form a stable interface with the water. Also, autoxidation had proceeded to the point where scission of the double bonds could have occurred making it very probable that the oxygen groups were in or near the surface of the monolayer.

5. The contact angle between methylene iodide and the monolayer was not greatly affected by autoxidation. Evidently, the size of the methylene iodide molecule prevented rapid diffusion of the methylene iodide through the unoxidized part of the monolayer. Also, the low affinity of the methylene iodide for the glass, relative to the affinity of the carboxyl group for the glass, prevented diffusion at the monolayer-glass interface. Thus, the contact angle was not influenced greatly by any changes in the mobility of the monolayer molecules which occurred during autoxidation.

Autoxidation of the monolayer on the glass surface was greatly affected by the presence of water vapor. The results of autoxidizing the monolayer in air at 50% relative humidity and the interpretation of these results were as follows:

1. Autoxidation was not effective in increasing the contact angle with water. Any water entrained in the autoxidized monolayer was removed by subsequent aging in dry air. The removal of the water did not increase the contact angle, indicating that the oxidized material was different from that produced in dry air.
2. Oxidation was not as extensive as in the dry air, and the material was more typical of the initial oxidation products formed during autoxidation of bulk systems. The products were probably monomeric and not capable of forming a solid-coherent structure which would form a stable interface with the water. Thus, the contact angle did not increase upon autoxidation.
3. Again, the contact angle between methylene iodide and the monolayer was not greatly affected by autoxidation as would be expected. However, the contact angle did increase slightly more than when the monolayers were aged in dry air. Evidently, a smaller decrease in the mobility of the

molecules was able to increase the contact angle more because oxygen groups were not introduced into the surface of the monolayer.

Monolayers were aged on copper in order to ascertain the effect of immobilizing the molecules through reaction of the carboxyl group with the copper. The results and their explanation were as follows:

1. The contact angle with water was about 86° immediately after deposition at which point 75% of the monolayer was insoluble in hexane. Thus, the water formed a high contact angle with the unoxidized linoleic acid monolayer if the molecules were immobilized.
2. As aging was carried out in dry air, the contact angle decreased to about 76.5° and remained constant upon further aging. Evidently, the angle decreased because hydrophilic oxygen groups were introduced into or near the surface of the monolayer due to scission of the double bonds.
3. Upon aging in the presence of water vapor, the contact angle increased from 86 to 92° as the reaction between the carboxyl group and the copper went to completion. Because the autoxidation was carried out under less severe conditions, scission of the double bonds evidently did not occur and the oxygen groups were not as accessible to the water. As a result, the contact angle was near that of water against a surface composed mostly of methylene groups such as polyethylene.

CONCLUSIONS

The effect of autoxidation of the linoleic acid monolayer on the contact angle with water depends upon the conditions of oxidation and the type of surface upon which the monolayer is formed. On a glass surface with which the carboxyl group cannot react, autoxidation increases the contact angle if it is extensive enough to form solid oxidation products. However, when the monolayer is formed upon a copper surface, with which the carboxyl group can react, the unoxidized molecules are already quite immobile. Then extensive autoxidation of the monolayer results in a decrease in the contact angle due to the introduction of oxygen containing functional groups into the monolayer surface.

The contact angle between methylene iodide and the monolayer formed on a glass surface is not greatly affected by autoxidation. The size of the molecule and its low affinity for the glass made it less susceptible to molecular motion in the monolayer. Thus, changes in the physical state of the monolayer which occur as a result of autoxidation have less of an effect on the contact angle.

SUGGESTIONS FOR FURTHER WORK

Autoxidation of monolayers of unsaturated fatty acids should be carried out under more varied conditions of aging. In particular, studies should be conducted to ascertain the influence of light, higher temperatures and the area per molecule on the surface. Of special interest is the effect of higher temperature. The products of autoxidation should contain less carbon-to-oxygen and more carbon-to-carbon linkages at higher temperatures. Thus, the oxidized material may be more effective in increasing the contact angle with water. Preliminary data support this conclusion. Two monolayers of linoleic acid were autoxidized at 95°C. for about 24 hours, and the contact angle with water was increased from zero to between 70 and 90 degrees. Such a study would produce information of practical significance. Fatty materials, suspected of contributing to the loss of absorbency, are frequently tested at elevated temperatures to accelerate the aging process. It is evident that such a practice might lead to erroneous conclusions, especially in the case of unsaturated fatty acids.

The experimental data showed that autoxidation of the monolayer was never complete. This may have been due to the inability of the reactants to diffuse on the surface. It would be interesting to simulate a free radical reaction using the computer assuming that the molecules were fixed on the surface in a definite pattern.

More work needs to be done in the area of the wettability of partial monolayers. The work of Bartell and Ruch (36, 37) needs to be extended using different solid surfaces, monolayers, and wetting liquids. In particular, a method should be developed for obtaining concentrations of less than a monolayer without resorting to the depletion of complete monolayers with organic solvents. Deposition of the monolayer while in an expanded state on the aqueous substrate may be one solution to the problem.

Evidently, the movement of fatty material over quite large distances is involved in the problem of self-sizing. However, apparently little work has been done to determine the rate of diffusion of fatty acids or their esters through or on the surface of cellulose. This would seem to provide an interesting and fruitful area for further research.

Admittedly, the above suggestions for further work cover only a small fraction of the interesting and useful studies which might be done in the field of sizing. However, they seem to be logical extensions of the work done in this thesis, and therefore were singled out for comment.

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APPENDIX I

SURFACE FILM BALANCE

A horizontal film balance was constructed to measure the relationship between the concentration of linoleic acid spread on the surface of a 0.01N HCl solution or distilled water and the surface tension of the substrate. The film balance was also used to transfer the linoleic acid monolayer to suitable solid surfaces.

The tray, as shown in Fig. 2, was made of lucite and a well, A, was placed in the bottom of the tray immediately in front of the float, B, so that glass slides could be lowered into the substrate when films were transferred to the surface. The lucite was covered with pressure-sensitive teflon tape and the seams of the tape were sealed with purified paraffin wax to prevent the water from dissolving the adhesive. The teflon made a good low energy surface and residual surface-active contaminants were removed by allowing water to set in the tray for about two weeks. The tray was supported by one-inch square brass rails, one under each edge of the tray. The tray was leveled with six leveling screws, three in each rail. The width of the tray was such that the float assembly used on the Cenco film balance could be attached to the tray.

The float assembly, C, provides a suspension for a torsion wire, D. To one end of the torsion wire was attached a vernier scale, E, which moves over a circular disk calibrated in degrees. The torsion wire was connected to a mica float which rests on the surface of the substrate. Thin, flexible platinum strips, F, were attached from the mica float to the edges of the float assembly such that the surface

the float displaces the float to the right (see Fig. 2). The float was then brought back to a zero position as indicated by the position of the pointer, G, by applying twist on the torsion wire. The difference in surface tension was measured directly from the vernier scale by calibrating the torsion wire. The torsion wire was calibrated by hanging known weights on a lever arm, H, which was at right angles to and the same distance from the torsion wire as the latter was from the float. The force was converted to dynes per cm. by dividing by the effective length of the float which was the length of the float plus one half of the width of the gap occupied by the platinum ribbons. The calibration constant for the torsion wire was 0.371 dynes per cm. degree of twist.

When operating the film balance, the tray was filled with the aqueous substrate until the surface was appreciably above the sides of the tray. The surface of the substrate was cleaned by sweeping with narrow glass plates, covered with teflon, from the float outward. The linoleic acid was spread on the surface to the left of the float and its concentration, expressed as the area per molecule, was changed by moving a barrier, I, towards the float. The difference in the surface tension between the clean surface and that containing the linoleic acid was correlated with the area per molecule of the linoleic acid.*

A theoretical basis for the study of insoluble fatty acid spread upon aqueous substrates can be developed from the Gibb's Adsorption Equation. Thus, a short discussion of this equation will be given. For a small reversible change in the internal energy of the system (13, 3)

*The number of molecules placed on the surface was known and the total area occupied by the linoleic acid was known from the distance of the barrier from the float and the width of the tray. Thus, the average area per molecule of the linoleic acid could be calculated.

$$dE = dE^{\alpha} + dE^{\beta} + dE^{s} \tag{37}$$

$$dE = TdS^{\alpha} + \mu_i dm_i - P^{\alpha}dV^{\alpha}$$
$$+ TdS^{\beta} + \mu_i dm_i - P^{\beta}dV^{\beta}$$
$$+ TdS^{s} + \mu_i dm_i^{s} + \gamma dA$$

where superscripts γ, β, $\underline{s}$ designate the two bulk phases and the surface phase, respectively:

$\underline{T}$ = temperature;

$\underline{S}$ = entropy;

$\underline{P}$ = pressure;

$\underline{V}$ = volume;

γ = surface tension;

$\underline{A}$ = area of interface;

$\underline{m_i}$ = mass of component $\underline{i}$

$\mu_{\underline{i}}$ = chemical potential of component $\underline{i}$.

If one bulk phase is air and the other an aqueous solution then the effect of air phase can be neglected and only the aqueous bulk phase considered. The extensive quantities attributed to the surface region are determined relative to some arbitrary dividing surface between the bulk phases. The extensive quantities for the surface region are computed and compared to the bulk system as a whole, and the properties of the surface region are related to any excess or deficiency of these quantities.

Now, considering just the surface region, Equation (37) reduces to

$$dE^{s} = TdS^{s} + \mu_i dm_i^{s} + \gamma dA \tag{38}$$

Integrating and fully differentiating it follows from Equation (38) that

$$0 = S^s dT + m_i{}^s d\mu_i + A d\gamma \tag{39}$$

or based upon unit area of surface

$$-d\gamma = S^s dT + \Gamma_i{}^s d\mu_i \tag{40}$$

where $\Gamma_{\underline{i}}^{\underline{s}}$ and $\underline{S}^{\underline{s}}$ are the excess quantities based upon unit area of surface. For a two-component system, such as a solvent, component one, and single solute, component two, Equation (40) becomes

$$-d\gamma = S^s dT + \Gamma_1{}^s d\mu_1 + \Gamma_2{}^s d\mu_2 \tag{41}$$

Since the dividing surface was drawn arbitrarily, it can be constructed so that there is no excess of the solvent, component one. Equation (41) now becomes

$$-d\gamma = S^s dT + \Gamma_2{}^s d\mu 2 \tag{42}$$

When the concentration of the solute molecules in the bulk phase is low and there is little interaction between the solute molecules in the surface region, the surface tension of the solution can be represented by a linear function of the concentration. Therefore,

$$\gamma_o - \gamma = bc_2 \tag{43}$$

where

γ_o = the surface tension of the pure solvent;

$\underline{c}_2$ = concentration of solute molecules.

Equation (42) may be written as

$$-d\gamma/dc_2 = \Gamma_2{}^s(kT/c_2) \tag{44}$$

However, as shown by Equation (43) $-\underline{d}\gamma/\underline{dc}_2 = \underline{b}$, so that Equation (44) is reduced to

$$(\gamma_o-\gamma)(\sigma) = kT \qquad (45)$$

or

$$\pi\sigma = kT$$

where

$$\sigma = 1/\Gamma_2^s$$

Equation (45) is the two-dimensional ideal gas law.

Very insoluble molecules spread on the surface of aqueous substrates approach this limiting relationship when the attractive forces between the molecules are quite small and the concentration on the surface is low (104, 105). By studying the way isotherms of π versus σ deviate from this limiting relationship, information has been gained as to the orientation of molecules on the surface, the size of molecules, and the nature of intermolecular forces.* Although π is measured by a difference in surface tension forces, it is convenient to consider that it arises from the translational energy of the molecules which cause an outward thrust. The system then becomes quite analogous to a three-dimensional system, and, as a result, certain conclusions can be drawn about the state of the molecules on the surface by comparing the π-σ isotherms with P-V isotherms.

The π-σ isotherms for a monolayer are shown in Fig. 30. The portion of the curve, EF, is representative of a solid monolayer. It is very incompressible and the area per molecule is close to the actual cross-sectional area of the molecule. ED represents a liquid condensed film which is characterized by a compressibility

*For very insoluble molecules it can be assumed that all the molecules placed on the surface remain there. Thus, σ can be calculated from the dimensions of the surface, and $(\gamma_o-\gamma)$ or π is measured experimentally.

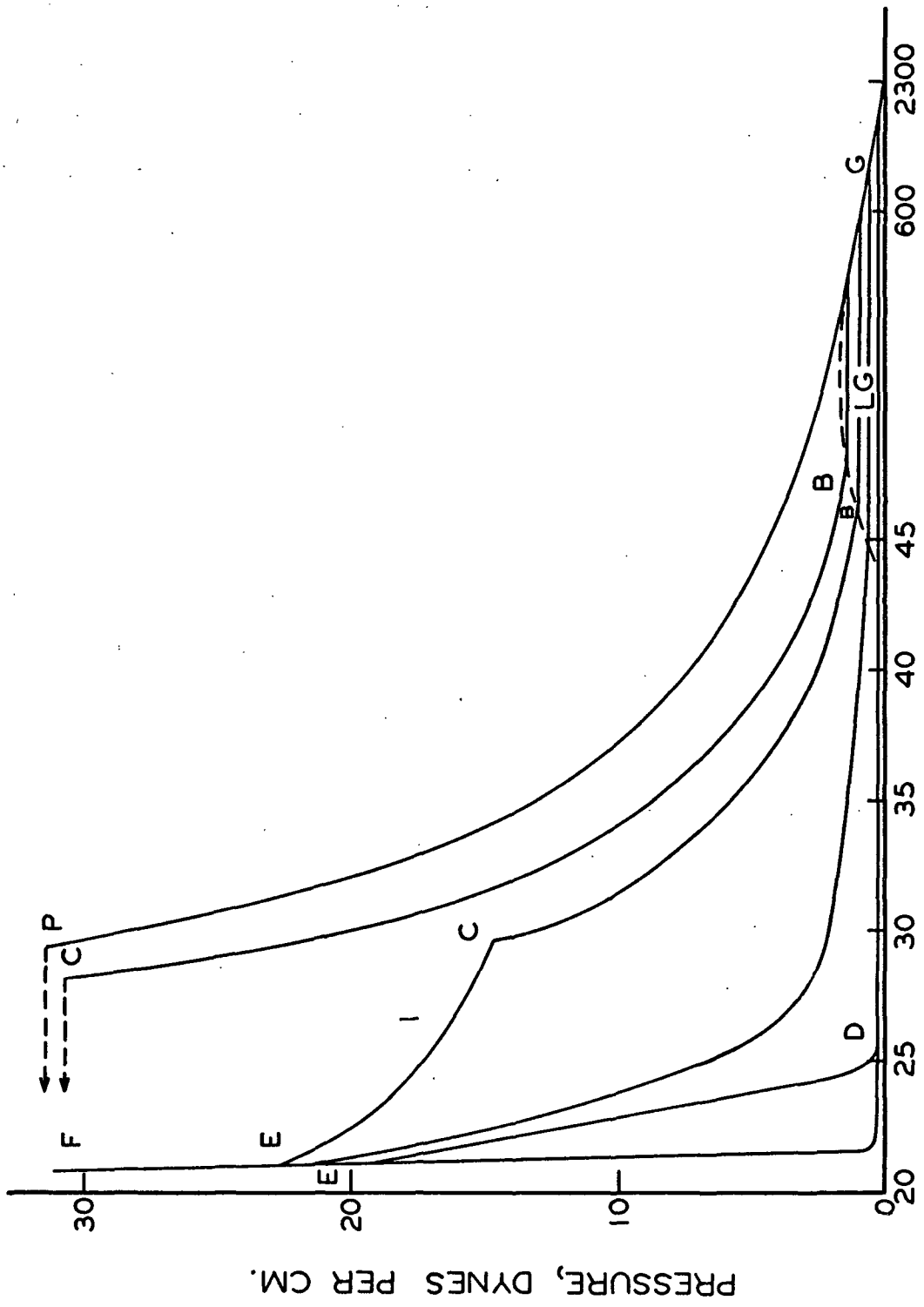

Figure 30. Pressure-Area Isotherms (105)

greater than the solid monolayer. However, it is still less than would be expected for a liquid monolayer where the molecules are in complete thermal motion. The liquid expanded state, CB, represents a nearly hyperbolic relationship. This is considered to be a liquid of very high compressibility. Lower molecular weight straight-chain acids such as lauric and myristic form such films at room temperature and low compression. However, upon compression, these films frequently exhibit a discontinuity in compressibility and pass from a liquid expanded state into an intermediate film, EC or I. Such a film then becomes solid upon further compression.

In the region enclosed by the dotted line, molecules in the two-dimensional gaseous state are in equilibrium with molecules in the liquid expanded phase. This is analogous in a three-dimensional system to a liquid in equilibrium with its vapor. At the point G, all the molecules are moving independently about the surface and the film is now gaseous. At higher temperatures the film may be above the critical point for this first-order transition to occur. Then the relationship moves along the line GP upon compression always remaining an expanded film until the point of collapse, dotted line.

APPENDIX II

LIST OF MATERIALS

LINOLEIC ACID

Five grams of linoleic acid were purchased from the Hormel Foundation, Austin, Minnesota. The methyl ester of the acid was prepared according to the method of Schlenk and Gellerman (126) as modified by Buchanan (127) and then analyzed by gas chromatography. The acid contained 1 to 1.5% of an impurity believed to be oleic acid. The supplier gave the following specifications with regards to purity.

Iodine Value: 181.0 (theoretical 181.03)

Conjugated polyunsaturated constituents from

U.V. absorption data:

Dienoic: not more than 0.10%
Trienoic: nil
Tetraenoic: nil

GLPC on methyl ester—only trace impurity visible.

Paper chromatogram: no visible contamination.

1-C^{14} LABELED LINOLEIC ACID

The labeled linoleic acid was obtained from the Volk Radio Chemical Company, Chicago, Illinois. The labeled linoleic acid was prepared by the method of Howton, et al., (128). The acid was purchased in three separate 0.05 millicurie quantities each with a specific activity of 15.9 mc./mM, and a weight of 0.88 mg. The acid was supplied in a benzene solution which was sealed in a vial. The specific activity of the labeled acid was adjusted to the proper value by dilution with the unlabeled acid. After dilution, the mixture was analyzed with reverse-phase chromatography. Scanning of the chromatogram with the ionization counter showed that about 3.5 to 4% of the labeled material moved with an R_f of about 0.2 as

compared with the R_f of about 0.5 for linoleic acid. The impurity was neutral since it was not extracted with caustic, and its concentration did not change upon oxidation of the linoleic acid. The manufacturer acknowledged that the 1-C^{14} linoleic acid may contain as much as 5% neutral material of unknown composition.

STEARIC ACID

The stearic acid was purchased from the Hormel Foundation, Austin, Minnesota. The specifications as to purity provided by the manufacturer were

iodine number: nil

melting point: 69.6°C.

1-C^{14} LABELED STEARIC ACID

The 1-C^{14} stearic acid was obtained from Volk Radio Chemical Company, Chicago, Illinois. The specific activity was 5.01 mc./mg. The acid was obtained in solid form in a vial.

OLEIC ACID

The oleic acid was a sample obtained from the Hormel Foundation, Austin, Minnesota. The specifications as to purity provided by the manufacturer were

Iodine number: 89.8
Per cent saturated: 0.20%
Per cent monoenoic: 99.39%
Per cent dienoic nonconjugated: 0.02%
Per cent trienoic: nil
Per cent tetraenoic: nil

WATER

All of the water used in the 0.01N hydrochloric acid substrate and for measuring the contact angle was redistilled from an alkaline potassium permanganate

solution. Approximately 0.5 g. of potassium permanganate and 1.25 g. of sodium hydroxide were added to 1500 ml. of distilled water. The water was redistilled from this solution occasionally adding new distilled water to maintain a constant total volume. A fresh solution of the permanganate was prepared when a considerable amount of manganese dioxide has been formed. The surface tension resistance of the redistilled water was 73.0 dynes/cm. at 22 $\pm$ 0.5°C. as measured with a du Noüy Tensiometer, and the specific resistance was 2.2×10^5 ohms at 25°C. The surface tension of water given in the literature is 72.44 dynes per cm. at 22°C. (16). The high reading was apparently an instrument error since the surface tension of the methylene iodide was high by about the same amount.

METHYLENE IODIDE

Methylene iodide from Fisher Scientific Company was repurified before it was used in the contact angle measurements. Two methods of purification were used. In one the methylene iodide was allowed to stand overnight over activated charcoal, and then passed through a column of alternating layers of charcoal and alumina until colorless. The methylene iodide was then stored in the refrigerator under nitrogen in the presence of a little mercury. The second method which gave the best results consisted of vacuum distilling the methylene iodide under nitrogen at a pressure of 0.8 mm. of mercury. The methylene iodide was stored over silver powder, under a blanket of nitrogen. Light was excluded by wrapping the flask in aluminim foil and the methylene iodide was kept in the solid state in the refrigerator. It was important to adhere to the above storage conditions in order to prevent decomposition. The methylene iodide is colorless when pure. The surface tension was 51.1 dynes/cm. at 22 $\pm$ 0.5°C. The surface tension of methylene iodide given in the literature was 50.76 dynes/cm. at 25°C. (16).

HEXANE

All of the hexane used was prepared by purifying practical-grade hexane obtained from the Matheson Coleman and Bell Company. It had a boiling point range from 65-69°C. The purification procedure was designed to remove any unsaturated or oxygenated impurities. The procedure was as follows (129):

> One thousand ml. of hexane, 60 ml. of 5% potassium permanganate solution, and 60 ml. of glacial acetic acid were placed in a 2000-ml. pyrex bottle and stirred vigorously under a hood for 90 minutes. The hexane layer was then decanted into a 2000-ml. separatory funnel and washed repeatedly with distilled water. A final wash consisted of about 100 ml. of 5% sodium carbonate solution. The hexane was then percolated through a 24-inch silica gel column to remove the polar compounds formed during the oxidation step.

The U.V. adsorption characteristics after purification are shown in Table XV.

TABLE XV

U.V. SPECTRUM OF PURIFIED HEXANE

Wavelength, mμ	Optical Density, 1 cm. path length
210	0.318
215	0.161
220	0.069
225	0.041
230	0.032
235	0.022
245	0.012
255	0.007
265	0.005

METHANOL

Reagent-grade methanol was purified by redistilling from zinc powder (130).

To 500 ml. of reagent-grade methanol were added 2.5 grams of potassium hydroxide and 6.25 grams of zinc powder. The mixture was refluxed in a hood on a steam bath for three hours. After refluxing, about 250 ml. of methanol was distilled and collected after discarding the initial 50 ml.

The U.V. spectrum of the purified methanol was as shown in Table XVI.

TABLE XVI

U.V. SPECTRUM OF PURIFIED METHANOL

Wavelength, mμ	Optical Density, 1 cm. path length
210	0.743
220	0.303
230	0.136
240	0.056
250	0.025
260	0.014
270	0.008
280	0.006
290	0.005
300	0.003

PARAFFIN WAX

Paraseal Canning Wax was purified to prevent surface-active impurities from contaminating the surface of the substrate. Polar, surface-active impurities were removed by passing the wax through a heated silica gel column. An electric heating tape was used for heating the silica gel column.

CALCIUM NITRATE

Analytical reagent, crystals, hydrate.

LITHIUM CHLORIDE

Analytical reagent, granular.

BENZENE

Analytical reagent, thiophene free.

MERCURY

Triple distilled, from Eastern Smelting and Refining Corporation.

HYDROGEN PEROXIDE

Analytical reagent, 30%.

HYDROCHLORIC ACID

Analytical reagent.

MINERAL OIL

Light mineral oil, George T. Walker and Company, was washed with water prior to use.

GLACIAL ACETIC ACID

Analytical reagent.

CHROMATOGRAPHIC PAPER

Whatman Number One.

ETHYL ETHER

U.S.P.

SILICA GEL

Silica gel grade 12, mesh size 28-200 from Davison Chemical, Baltimore 3, Maryland.

SILVER METAL

Precipitated powder, certified reagent, from Fisher Scientific Company.

APPENDIX III

NITROGEN BOX

A gloved nitrogen box was constructed of stainless steel with safety glass panels in the top and front (see Fig. 31). A water lock was provided at one end so that items could be moved in and out of the box without destroying the oxygen-free atmosphere. Values and an electrical outlet were provided in the back.

The oxygen was removed from the atmosphere at room temperature by the prcce-dure of Altieri (131). The gas in the box was circulated with a Randolph pump over copper turnings which were continuously washed with an ammoniacal ammonium chloride solution. The copper removed the oxygen from the atmosphere through the formation of copper oxide, and the copper surface was continually regenerated by solution of the copper oxide by the ammonium chloride solution. After passing over the copper turnings, the gas was washed successively with two dilute sulfuric acid solutions and water and then returned to the box. The atmosphere in the box was maintained under a positive pressure of 0.25 inch of water by a small continuous bleed of nitrogen. When in use the oxygen content of the atmosphere was kept below 0.1% as measured by an Orsat apparatus.

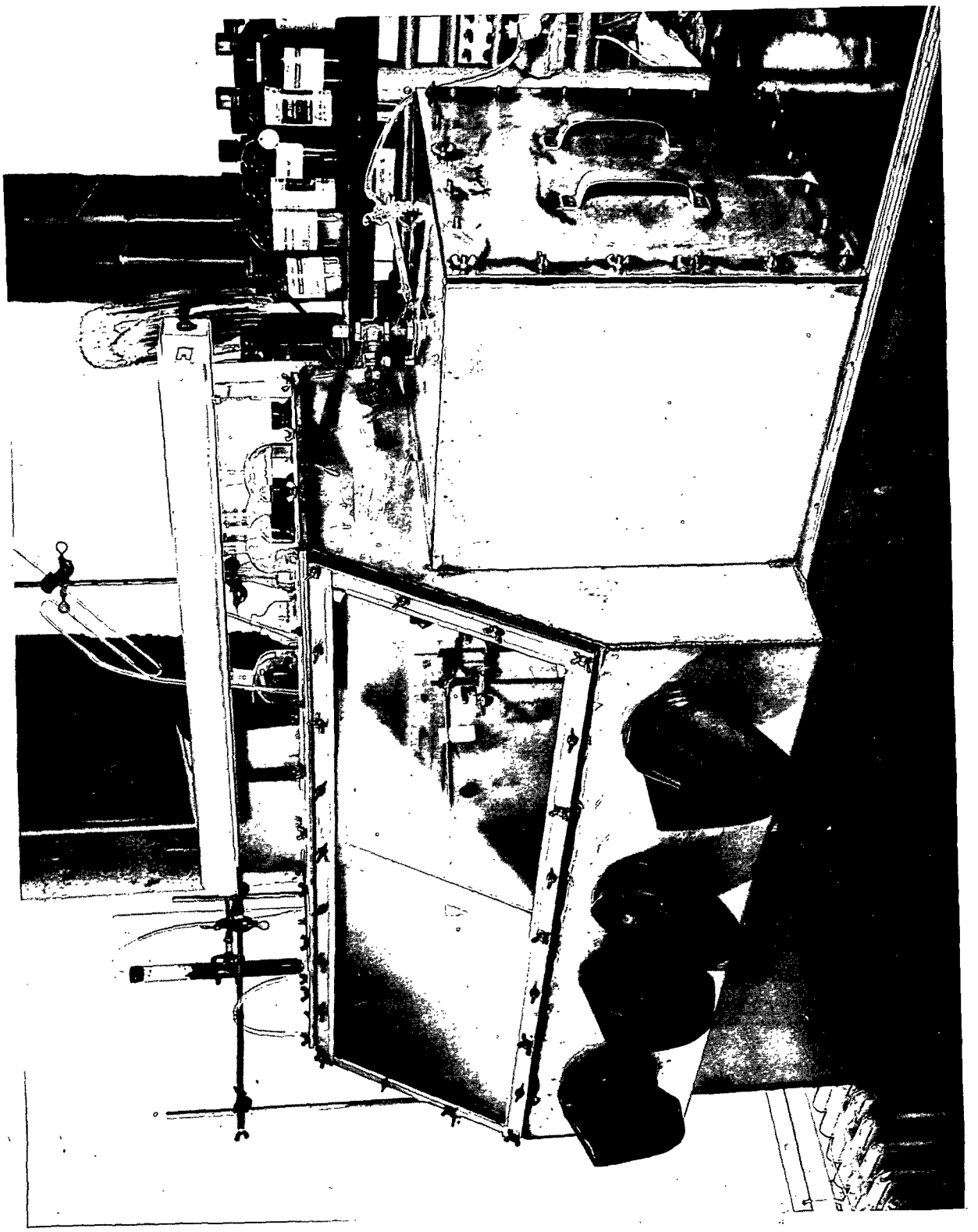

Figure 31. Nitrogen Box

APPENDIX IV

CLEANING OF SOLID SURFACES

The glass slides were cleaned with a hydrochloric acid-hydrogen peroxide mixture. This cleaning solution was used because it was not supposed to attack the glass and the presence of heavy metal ions was kept to a minimum. The cleaning solution was 6% hydrochloric acid and 6% hydrogen peroxide. The slides were first marked with a vibra tool across the width of the slides and 15 mm. from one end. They were then placed in a horizontal staining dish and immersed in the cleaning solution for 24 to 48 hours. The slides were washed with cold distilled water followed by hot distilled water. During the hot wash the surfaces were rubbed with cotton to remove any loose material not dissolved. The hot rinse was followed by another cold water rinse. The water was then drained away and the slides left in the covered staining dish until used (within 1 to 2 hours). After cleaning, the surface was completely wet with water and no breakup of the water film was noted upon drying.

Relatively smooth copper surfaces were prepared by polishing 3 by 1-inch copper plates. The surfaces were cleaned by first polishing with Shamva until free of copper oxide. After rinsing with water and drying, the plates were subsequently boiled in benzene for one to two hours. When used the plates were removed from the hot benzene and the excess benzene allowed to evaporate. The remaining benzene monolayer was removed by flaming the plate gently in a blue flame until a light brown oxide film had formed. The slide was then immediately immersed in distilled water. When the plate was immersed in the 0.01N hydrochloric acid substrate, the oxide film was removed.

APPENDIX V

PREPARATION OF SOLUTIONS

Two unlabeled linoleic acid solutions were prepared in concentrations of 0.874×10^{-2} and 0.874×10^{-3} M. Three milliliter and three-tenths milliliter of a 7.26×10^{-2} M linoleic acid in benzene solution were pipetted into 25-milliliter volumetric flasks and the benzene evaporated under nitrogen. The volume was made up to the mark with hexane. The solutions were used to spread unlabeled linoleic acid monolayers on the 0.01N hydrochloric acid substrate for determining the pressure area isotherm. The unlabeled oleic acid solution for measuring the pressure-area isotherm was prepared in a similar manner as the linoleic acid solutions and the concentration was 0.931×10^{-3} M.

Three labeled linoleic acid–hexane solutions were prepared. The vial containing the labeled acid was wiped clean with benzene before opening. The tip on the vial was broken open and the benzene evaporated under nitrogen. The labeled acid was dissolved in hexane and transferred to a volumetric flask. The unlabeled linoleic acid was pipetted from a stock hexane solution into the volumetric flask and the volume made up with hexane. Three labeled solutions were prepared, two with specific activities of 3.35 μc./mg. and one with a specific activity of 6.43 μc./mg. based upon the data on the labeled acid supplied by the manufacturer. The total concentration was 1.17×10^{-3} M for the less active solutions and 1.11×10^{-3} M for the more active solution.

The labeled stearic acid was prepared by weighing suitable proportions of labeled and unlabeled stearic acid into a weighing bottle on a semimicro balance, transferring the mixture to a volumetric flask and making up to volume with hexane. The final concentration was 1.08×10^{-3} M and the specific activity 6.16 μc./mg.

The aqueous substrate was prepared by making up a 0.1N hydrochloric acid solution in a 1000-ml. volumetric flask using hydrochloric acid concentrate and redistilled distilled water. One hundred milliliters of the 0.1N solution was pipetted into a 1000-ml. volumetric flask and made up to volume with redistilled water to produce the 0.01N hydrochloric acid solution which was used as the aqueous substrate upon which to spread the monolayer.

APPENDIX VI

CALCULATIONS

AREA PER MOLECULE OF THE LINOLEIC ACID

The area per molecule of the linoleic acid on the glass surface was calculated from the count of a stearic acid monolayer of known specific activity. The derivation of the relationship was as follows:

Let: $\underline{x}_1$ = the specific activity of the linoleic acid on a weight basis;

$\underline{x}_2$ = the specific activity of the stearic acid on a weight basis;

$\underline{Y}_1$ = the weight of linoleic acid covering the surface;

$\underline{Y}_2$ = the weight of stearic acid covering the surface;

$\underline{K}_1$ = the proportionality constant between the total number of disintegrations of the labeled linoleic acid and the count;

$\underline{K}_2$ = the proportionality constant between the total number of disintegrations of the labeled stearic acid and the count;

$\underline{Z}_1$ = the count of the linoleic acid monolayer;

$\underline{Z}_2$ = the count of the stearic acid monolayer;

σ_1 = the area per molecule of the linoleic acid;

σ_2 = the area per molecule of the stearic acid;

$\underline{M}_1$ = the molecular weight of the linoleic acid;

$\underline{M}_2$ = the molecular weight of the stearic acid;

$\underline{N}$ = Avogadro's number;

$\underline{A}_1$ = the total surface area of the glass slide available to the linoleic acid;

$\underline{A}_2$ = the total surface area of the glass slide available to the stearic acid.

The count of the monolayers is given by the following equations:

$$Z_1 = (K_1)(X_1)(Y_1) \tag{46}$$

$$Z_2 = (K_2)(X_2)(Y_2) \tag{47}$$

By assuming that $\underline{K}_1$ is equal to $\underline{K}_2$, the ratio of the above equations is

$$Z_1/Z_2 = (X_1)(Y_1)/(X_2)(Y_2) \tag{48}$$

However,

$$Y_1 = (A_1)(M_1)/(\sigma_1)(N) \tag{49}$$

$$Y_2 = (A_2)(M_2)/(\sigma_2)(N) \tag{50}$$

Upon substitution of Equations (49) and (50) into Equation (48) and rearranging, assuming that $\underline{A}_1$ is equal to $\underline{A}_2$, the following equation is obtained

$$\sigma_1 = (X_1)(M_1)(\sigma_2)(Z_2)/(X_2)(M_2)(Z_1) \tag{51}$$

Equation (51) was evaluated as follows to obtain the area per molecule of the linoleic acid in the most compact monolayer on the glass surface.

$$\sigma_1 = \frac{(3.33 \text{ c./mg.})(280.4)(20.5 \text{ A.}^2)(3{,}365 \text{ c.p.m.})}{(6.16 \text{ c./mg.})(284.5)(1{,}213 \text{ c.p.m.})}$$

$$\sigma_1 = 30.5 \text{ A.}^2$$

SPREADING OF MONOLAYER MOLECULES ON THE DROP SURFACE

Order of magnitude calculations were made to ascertain how much of the monolayer under the drop would have to spread on the drop surface in order to decrease the surface tension of the water 5 dynes per cm. It was assumed that the drop was approximately spherical and that molecules which spread upon the water surface came

only from that portion of the monolayer which was under the drop. It was also assumed that the area under the drop was equal to the geometric area and the concentration of the molecules on the drop surface when the surface tension was decreased 5 dynes per cm. was given by the pressure-area isotherm of the linoleic acid on distilled water.

Let: $\underline{X}$ = the total number of molecules which spread on the drop surface;

$\underline{Y}$ = the total number of molecules which initially occupied the area covered by the drop;

$\underline{A}$ = the area of the drop surface;

$\underline{a}$ = the diameter of the drop at the monolayer-drop interface;

$\underline{h}$ = the height of the drop;

σ_1 = area per molecule in the monolayer = 30.5 $A.^2$

σ_2 = area per molecule on the drop surface = 45.3 $A.^2$

θ = the contact angle.

The per cent of the monolayer under the drop which has to spread on the surface in order to lower the surface tension 5 dynes per cm. is given by the following equation:

$$\% = (100)(X)/(Y) = (100)(A)(\sigma_1)/(\pi a^2/4)(\sigma_2) \qquad (52)$$

The value of $\underline{A}$ is given by the following equation:

$$A = (\pi/4)(4h^2+a^2) \qquad (53)$$

Combining Equations (52) and (53) leads to the following:

$$\% = (100)(\sigma_1)(4h^2+a^2)/(a^2)(\sigma_2) \qquad (54)$$

When the drop is spherical, the contact angle is related to the $\underline{h}$ and $\underline{a}$ by the following equation:

$$\text{Tan } (1/2\theta) = 2h/a \qquad (55)$$

Substitution of Equation (55) into Equation (54) and cancelling of terms leads to

$$\% = (200)(\sigma_1)/(1+\text{cosine } \theta)(\sigma_2) \qquad (56)$$

Using Equation (56), the amount of the monolayer which would have to spread on the drop surface was calculated for various degrees of autoxidation of the monolayer. The results are shown in Table XVII.

TABLE XVII

AMOUNT OF THE MONOLAYER WHICH SPREADS ON THE DROP SURFACE

Amount of Autoxidation, %	Contact Angle, degrees	Amount Spread on Surface, %
20	16.6	69
30	30.7	73
40	39.8	76
50	47.3	80
60	53.1	84

APPENDIX VII

EXPERIMENTAL DATA

TABLE XVIII

PRESSURE-AREA ISOTHERM OF LINOLEIC ACID ON 0.01N HCl[a]

Distance of Barrier from Float, cm.	Area per Molecule, $A.^2$	Twist on Torsion Wire, degrees	Film Pressure, dynes/cm.
22	23.4	80.8	29.4
24	25.5	80.7	29.4
26	27.7	80.7	29.4
28	29.8	80.7	29.4
30	31.9	72.4	26.3
32	34.1	59.0	21.5
34	36.2	47.8	17.4
36	38.3	38.3	13.9
38	40.4	28.8	10.5
40	42.6	22.8	8.3
42	44.7	18.5	6.7
44	46.8	14.7	5.4
46	48.9	11.5	4.2
48	51.1	9.3	3.4

[a]Concentration of spreading solution: 0.874×10^{-2} M.
Amount added to surface: 25λ.
Calibration constant of torsion wire: 0.3637 dyne, $cm.^{-1}$, $degree^{-1}$.
Inside width of tray: 14.0 cm.

TABLE XIX

PRESSURE-AREA ISOTHERM OF LINOLEIC ACID ON 0.01N HCl[a]

Distance of Barrier from Float, cm.	Area per Molecule, $A.^2$	Twist on Torsion Wire, degrees	Film Pressure, dynes/cm.
18	23.9	81.5	29.6
20	26.6	81.5	29.6
22	29.3	81.2	29.5
24	31.9	70.8	25.8
26	34.6	54.1	19.7
28	37.2	41.3	15.0
30	39.9	32.2	11.7
32	42.6	23.5	8.6
34	45.2	17.4	6.3
36	47.9	13.1	4.8
38	50.5	9.8	3.6
40	53.2	7.2	2.6
42	55.9	5.3	1.9
44	58.5	3.7	1.4
46	61.2	2.7	1.0
48	63.8	1.6	0.6

[a]Concentration of spreading solution: 0.874×10^{-3} M.
Amount added to surface: 200λ.
Calibration constant of torsion wire: 0.3637 dyne, $cm.^{-1}$, $degree^{-1}$.
Inside width of tray: 14.0 cm.

TABLE XX

PRESSURE-AREA ISOTHERM OF LINOLEIC ACID ON DISTILLED WATER[a]

Distance of Barrier from Float, cm.	Area per Molecule, $A.^2$	Twist on Torsion Wire, degrees	Film Pressure, dynes/cm.
10	21.0	80.3	29.8
11	23.1	79.8	29.6
12	25.2	79.0	29.3
13	27.3	77.2	28.6
14	29.4	67.3	25.0
15	31.5	55.3	20.5
16	33.6	46.1	17.1
17	35.7	37.9	14.1
18	37.8	30.6	11.4
20	42.6	20.3	7.5
22	46.2	12.2	4.5
24	50.4	7.7	2.9
26	54.6	4.2	1.6
28	58.8	2.8	1.0
30	63.0	2.7	1.0
32	67.2	2.7	1.0
36	75.6	2.6	1.0

[a]Concentration of spreading solution: 1.06×10^{-3} M.
Amount added to surface: 100λ.
Calibration constant of torsion wire: 0.371 dyne, $cm.^{-1}$, $degree^{-1}$.
Inside width of tray: 13.4 cm.

TABLE XXI

PRESSURE-AREA ISOTHERM OF OLEIC ACID ON 0.01N HCl[a]

Distance of Barrier from Float, cm.	Area per Molecule, $A.^2$	Twist on Torsion Wire, degrees	Film Pressure, dynes/cm.
18	22.5	84.4	30.7
20	25.0	84.2	30.6
22	27.5	83.4	30.3
24	30.0	81.0	29.5
26	32.5	62.9	22.9
28	34.9	47.0	17.1
30	37.4	35.1	12.8
32	39.9	24.4	8.9
34	42.4	17.8	6.5
36	44.9	12.0	4.4
38	47.4	8.0	2.9
40	49.9	4.6	1.7
42	52.4	2.2	0.8
44	54.9	1.7	0.6

[a]Concentration of spreading solution: 0.931×10^{-3} M.
Amount added to surface: 200λ.
Calibration constant of torsion wire: 0.3637 dyne, $cm.^{-1}$, $degree^{-1}$.
Inside width of tray: 14.0 cm.

TABLE XXII

RADIOACTIVE COUNT OF THE LINOLEIC ACID MONOLAYER AS A FUNCTION OF THE DEPOSITION PRESSURE

Monolayer No.	Film Pressure, dynes/cm.	Area per Molecule, $A.^2$	Solid Surface	Radioactive Count, c.p.m.
50-6	28.2	31.0	glass	1,669
50-5	27.5	31.3	glass	1,427
50-1	18.6	35.3	glass	1,126
50-2	11.1	40.1	glass	971
50-3	3.7	49.9	glass	755
73-3	26.0	31.9	unflamed copper	1,276[a]
71-1	26.0	31.9	flamed copper	3,426[a]
71-2	22.3	33.0	flamed copper	2,107[a]
71-3	14.8	37.4	flamed copper	1,262[a]
73-1	11.1	40.1	flamed copper	1,043[a]
72-1	7.4	43.8	flamed copper	823[a]
72-3	3.7	49.9	flamed copper	740[a]

[a]Radioactive count was corrected for the increased backscattering of the copper relative to that of the glass.

TABLE XXIII

RADIOACTIVE COUNT OF THE STEARIC ACID MONOLAYER

Monolayer No.	Film Pressure, dynes/cm.	Solid Surface	Radioactive Count, c.p.m.
16-4	27.8	glass	3,441
17-1	27.8	glass	3,369
17-2	27.8	glass	3,310
17-3	27.8	glass	3,351
17-4	27.8	glass	3,352
73-2	27.8	flamed copper	3,886[a]

[a]Radioactive count was not corrected for the increased backscattering relative to that for glass.

TABLE XXIV

CONTACT ANGLE BETWEEN WATER AND THE AUTOXIDIZED MONOLAYER[a]

Monolayer No.	Time of Aging, hours	Autoxidation, %	Contact Angle, degrees
52-1	10	15.0	17
52-2	8	43.5	42
52-3	5	39.5	40
52-4	23	20.4	13
52-5	8	18.3	16
52-6	43	63.7	56
53-1	3	38.4	32
53-2	25	27.9	29
54-1	19	61.7	53
54-2	20	27.3	30
54-3	30	24.2	14
54-4	40	25.0	21
54-6	60	22.1	23
55-5	37	21.5	15
55-6	72	20.4	9
56-1	59	19.3	21
56-2	191	22.1	7
57-1	72	25.1	26
57-2	28	55.3	49
57-3	189	67.1	57
57-5	20	30.6	25
58-1	171	34.2	38
58-3	189	29.9	28
58-4	191	38.8	39
59-2	72	29.1	38
59-3	76	66.1	52
59-4	75	58.3	55
59-5	94	31.4	38
60-3	54	52.1	50

[a]Monolayers aged in dry air.

TABLE XXIV (continued)

CONTACT ANGLE BETWEEN WATER AND THE AUTOXIDIZED MONOLAYER[a]

Monolayer No.	Time of Aging, hours	Autoxidation, %	Contact Angle, degrees
60-4	54	31.6	29
60-5	125	33.6	42
60-6	125	65.0	58
76-1	19	22.9[b]	13
76-3	123	35.6[b]	29
76-5	153	45.8[b]	41
76-6	336	41.0[b]	44
79-1	79	15.6[b]	11
79-4	290	59.2[b]	53
79-5	311	55.5[b]	50
80-1	297	38.3[b]	41
80-2	387	51.4[b]	50
93-1, 93-2	743	60.0[b]	53

[a]Monolayers aged in dry air.

[b]Degree of autoxidation was determined by chromatography. All other values were determined by hexane insolubility.

TABLE XXV

CONTACT ANGLE WITH ONLY THE MATERIAL PRODUCED DURING AUTOXIDATION[a]

Monolayer No.	Concentration of Material on Surface, % of a monolayer	Contact Angle, degrees Water	Methylene Iodide
52-1	15.0	23	41
52-2	43.5	45	46
52-3	39.5	42	46
52-4	20.4	22	42
52-5	18.3	25	41
52-6	63.7	56	47
53-1	38.4	35	46
53-2	27.9	35	44
54-3	24.2	24	43
54-4	25.0	28	42
54-6	22.1	31	43
55-5	21.5	20	42
55-6	20.4	19	42
56-1	19.3	28	41
56-2	22.1	9	42
57-1	25.1	32	42
57-2	55.3	49	47
57-3	62.7	55	45
57-5	30.6	32	42
58-1	33.5	39	44
58-3	30.1	34	41
58-4	38.3	43	43
59-2	28.9	41	42
59-3	65.0	54	44
59-4	59.8	57	46
59-5	32.5	43	42
60-3	51.5	52	45
60-4	33.1	29	42
60-5	32.2	42	45
60-6	59.6	58	44

[a]Monolayers aged in dry air.

TABLE XXVI

CONTACT ANGLE BETWEEN METHYLENE IODIDE AND THE AUTOXIDIZED MONOLAYER[a]

Monolayer No.	Time of Aging, hours	Autoxidation,[b] %	Contact Angle, degrees
64-1	18	39.5	46
64-2	18	57.4	45
64-3	43	58.2	45
64-4	43	26.2	44
64-5	62	44.5	44
64-6	62	30.4	45
65-1	67	48.2	44
65-2	66	29.7	45
65-3	90	23.1	44
65-4	91	65.1	47
66-1	0	15.7	44
66-2	0	16.5	43

[a]Monolayers aged in dry air.

[b]Degree of autoxidation determined by hexane insolubility.

TABLE XXVII

CONTACT ANGLE BETWEEN METHYLENE IODIDE AND THE AUTOXIDIZED MONOLAYER[a]

Monolayer No.	Amount Insoluble in Hexane, %	Contact Angle, degrees
82-1	28.2	45
82-2	43.2	47
82-3	41.7	47
82-4	64.6	48
83-1	37.9	47
83-2	55.3	48
83-3	60.2	49
83-4	64.4	47
83-5	71.6	49

[a]Monolayer aged in air of 50% relative humidity.

TABLE XXVIII

CONTACT ANGLE BETWEEN WATER AND THE MONOLAYER AUTOXIDIZED ON A COPPER SURFACE

Monolayer No.	Time of Aging, hours	Contact Angle, degrees
81-1[a]	0.0	85.6
81-1	6.4	85.6
81-1	17.9	83.3
81-1	43.2	79.4
81-1	89.7	74.6
81-1	138.3	74.8
81-1	186.6	75.2
81-3[a]	0.9	87.2
81-3	12.7	84.2
81-3	37.8	76.3
81-3	84.9	78.4
81-3	132.9	75.8
81-3	183.4	77.8
81-2[b]	0.1	86.8
81-2	14.1	88.7
81-2	39.3	89.5
81-2	86.5	91.9
81-2	134.9	92.1
81-2	186.6	90.2

[a]Monolayer aged in dry air.

[b]Monolayer aged in air of 50% relative humidity.

TABLE XXIX

RATE OF AUTOXIDATION IN AIR OF 50% RELATIVE HUMIDITY

Monolayer No.	Time of Aging, hours	Amount of Monolayer Autoxidized, %
92-4	0.0	22.5
92-5	0.0	23.1
82-1	5.8	28.2
83-1	22.6	37.9
82-2	26.1	43.2
82-3	42.8	41.7
83-2	76.2	55.3
82-4	89.5	64.6
83-3	119.6	60.2
83-4	169.0	64.4
83-5	191.5	71.6
90-1	148.2	34.0[a]
90-2	148.9	33.5[a]
95-3, 95-4	150.6	36.2[a]
95-1, 95-2	170.7	34.5[a]
90-3	194.0	41.5[a]

[a]Degree of autoxidation was determined by chromatography. All other values were determined by hexane insolubility.

TABLE XXX

THE EFFECT OF AGING OF THE MONOLAYER IN NITROGEN OF 50% RELATIVE HUMIDITY ON THE AMOUNT INSOLUBLE IN HEXANE

Monolayer No.	Time of Aging, hours	Amount Insoluble in Hexane, % of a monolayer
37-2	24.0	19.5
38-5	24.0	24.4
38-4	29.4	22.9
37-1	48.3	25.4
37-3	96.0	27.7
38-2	96.0	22.6
38-1	135.5	29.7